4324 *Inorg. Chem.* **1993**, *32,* 4324–4336

1,3-Diaryltriazenido Compounds of Aluminum

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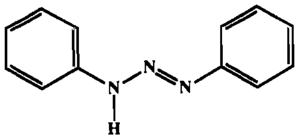
Received March 5, 1993®

Reaction of $\mathrm{AlH(^iBu)_2}$ with 1 and 2 equiv of 1,3-diphenyltriazene, (Ph)NNN(H)(Ph), yields $\mathrm{Al(^iBu)_2[N(Ph)NN(Ph)]}$ (**1**) and $\mathrm{Al(^iBu)[N(Ph)NN(Ph)]_2}$ (**2**), respectively. Compound **2** undergoes ligand exchange in solution to give an equimolar mixture of **1** and $\mathrm{Al[N(Ph)NN(Ph)]_3}$. The reaction of $\mathrm{Al(^tBu)_3}$ with (Ph)NNN(H)(Ph) gives $\mathrm{Al(^tBu)_2[N(Ph)NN(Ph)]}$ (**3**) as the only product. Addition of 1 equiv of (Ph)NNN(H)(Ph) to $\mathrm{AlMe_2(BHT)(OEt_2)}$ (BHT–H = 2,6-di-*tert*-butyl-4-methylphenol) allows for the isolation of AlMe(BHT)[N(Ph)NN(Ph)] (**4**); however, higher equivalents of (Ph)NNN(H)(Ph) yield only $\mathrm{Al[N(Ph)NN(Ph)]_3}$. The bis(triazenide) complex $\mathrm{Al(BHT)[N(Ph)NN(Ph)]_2}$ (**5**) is isolated from the reaction of (Ph)NNN(H)(Ph) with $\mathrm{AlH_2(BHT)(NMe_3)}$, while $\mathrm{Al(BHT)_2[N(Ph)NN(Ph)]}$ (**6**) is formed from the reaction of (Ph)NNN(H)(Ph) with $\mathrm{AlMe(BHT)_2}$. Although the reaction of **1** with $\mathrm{H_2salen}$ [*N,N'*-ethylenebis(salicylideneamine)] does not yield Al[N(Ph)NN(Ph)](salen) (**8**) but rather yields $\mathrm{Al(^iBu)(salen)}$ (**7**), compound **8** may be isolated from interaction of (Ph)NNN(H)(Ph) with AlMe(salen). The reaction between $\mathrm{AlMe_3}$ and 3 equiv of substituted 1,3-diaryltriazenes, (Ar)NNN(H)(Ar), yields the 6-coordinate aluminum tris(1,3-diaryltriazenido) compounds, $\mathrm{Al[N(Ar)NN(Ar)]_3}$ [Ar = 2-MePh (**9**), 4-MePh (**10**), 4-MeOPh (**11**), 4-FPh (**12**), 4-ClPh (**13**), 4-BrPh (**14**), $\mathrm{C_6F_5}$ (**15**)]. The unsymmetrical diaryltriazene complex $\mathrm{Al[N(Ph)NN(4\text{-}MeOPh)]_3}$ (**16**) adopts a *trans*-meridional conformation. The spectroscopic characterization of the tris(triazenido) complexes is discussed with respect to the nature of the aryl substituents. The X-ray structures of **1**, **6**, AlMe(salen), **9**, **11**, **13**, $\mathrm{(C_6F_5)NNN(H)(C_6F_5)}$, and $\mathrm{(2\text{-}MePh)NNN(H)(2\text{-}MePh)\cdot(2\text{-}MePh)NH_2}$ have been determined. Crystallographic data for **1**: monoclinic, $P2_1/c$, $a = 12.437(7)$ Å, $b = 12.327(5)$ Å, $c = 13.413(9)$ Å, $\beta = 98.29(5)°$, $Z = 4$, $R = 0.059$, $R_w = 0.071$. Crystallographic data for **6**: monoclinic, $C2/c$, $a = 17.967(b)$ Å, $b = 10.030(5)$ Å, $c = 21.650(6)$ Å, $\beta = 99.99(2)°$, $Z = 2$, $R = 0.086$, $R_w = 0.090$. Crystallographic data for AlMe(salen): monoclinic, $P2_1/n$, $a = 11.751(8)$ Å, $b = 12.227(9)$ Å, $c = 12.609$ Å, $\beta = 98.52(6)°$, $Z = 4$, $R = 0.082$, $R_w = 0.082$. Crystallographic data for **9**: monoclinic, $P2_1/c$, $a = 11.392(3)$ Å, $b = 11.418(3)$ Å, $c = 31.227(9)$ Å, $\beta = 94.31(2)°$, $Z = 4$, $R = 0.093$, $R_w = 0.099$. Crystallographic data for **11**: tetragonal, $I4_1/a$, $a = 27.996(6)$ Å, $c = 20.613(5)$ Å, $Z = 16$, $R = 0.076$, $R_w = 0.077$. Crystallographic data for **13**: monoclinic, $P2_1/c$, $a = 8.746(3)$ Å, $b = 18.754(4)$ Å, $c = 22.985(5)$ Å, $\beta = 90.36(3)°$, $Z = 4$, $R = 0.042$, $R_w = 0.056$. Crystallographic data for $\mathrm{(C_6F_5)NNN(H)(C_6F_5)}$: monoclinic, $P2_1/c$, $a = 10.027(4)$ Å, $b = 9.909(4)$ Å, $c = 12.998(4)$ Å, $\beta = 96.00(3)°$, $Z = 4$, $R = 0.034$, $R_w = 0.046$. Crystallographic data for $\mathrm{(2\text{-}MePh)NNN(H)(2\text{-}MePh)\cdot(2\text{-}MePh)NH_2)}$: triclinic, $P1$, $a = 9.609(9)$ Å, $b = 10.272(5)$ Å, $c = 11.276(5)$ Å, $\alpha = 108.53(8)°$, $\beta = 114.90(7)°$, $\gamma = 90.88(7)°$, $Z = 2$, $R = 0.070$, $R_w = 0.070$.

Introduction

The first extensive investigation of the coordination chemistry of 1,3-diphenyltriazene (I) was carried out over 100 years ago by Meldola.[1] While in the intervening years numerous transition metal triazenide compounds have been studied, only limited examples of group 13 triazenides have appeared.[2-5]



(I)

In a previous publication[6] we described the X-ray structural characterization of the aluminum 1,3-diphenyltriazenido complex $\mathrm{Al[N(Ph)NN(Ph)]_3}$ (**II**). Although we initially prepared $\mathrm{Al[N(Ph)NN(Ph)]_3}$ from the reaction of $\mathrm{AlMe_3}$ with 3 equiv of 1,3-diphenyltriazene (eq 1), we showed that the tris complex was

$$\mathrm{AlMe_3 + 3(Ph)NNN(H)(Ph) \longrightarrow Al[N(Ph)NN(Ph)]_3 + 3MeH} \quad (1)$$

the sole product isolated even when a large excess of $\mathrm{AlMe_3}$ was employed.[7] If, however, the reaction is carried out in the presence of a strong Lewis base, such as 3,5-dimethylpyridine

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® Abstract published in *Advance ACS Abstracts,* August 15, 1993.

[1] (a) Meldola, R.; Streatfield, F. W. *J. Chem. Soc.* **1887**, 434. (b) Meldola, R.; Streatfield, F. W. *J. Chem. Soc.* **1888**, 664. (c) Melodola, R.; Streatfield, F. W. *J. Chem. Soc.* **1890**, 785.

[2] (a) Black, D. St. C.; Davis, V. C.; Deacon, G. B.; Schultze, R. J. *Inorg. Chim. Acta* **1979**, *37*, L528. (b) Beck, J.; Strahle, J. *Z. Naturforsch., B* **1986**, *41*, 1381.

[3] (a) Brinckman, F. E.; Haiss, H. S. *Chem. Ind.* **1963**, 1124. (b) Brinckman, F. E.; Haiss, H. S.; Robb, R. A. *Inorg. Chem.* **1965**, *4*, 936.

[4] Wheeler, P. P.; Richardson, A. C. *Mikrochim. Ichnoanal. Acta* **1964**, 609.

[5] Coates, G. E. Mukherjee, R. N. *J. Chem. Soc.* **1964**, 1295.

[6] Leman, J. T.; Barron, A. R.; Ziller, J. W.; Kren, R. M. *Polyhedron* **1989**, *8*, 1909.

[7] $\mathrm{Al[N(Ph)NN(Ph)]_3}$ may also be prepared by the reaction of $\mathrm{AlCl_3}$ with 3 equiv of Ag[N(Ph)NN(Ph)]; see ref 4a.

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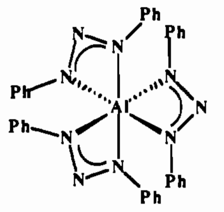
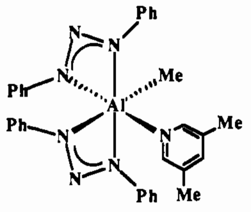
(3,5-$\mathrm{Me_2py}$), a less highly substituted compound can be isolated (eq 2).[8] X-ray crystallographic characterization of

$$\mathrm{AlMe_3 + 2(Ph)NNN(H)(Ph)} \longrightarrow \overline{\mathrm{AlMe[N(Ph)NN}}\mathrm{(Ph)]_2(3,5\text{-}Me_2py) + 2MeH} \quad (2)$$

$\overline{\mathrm{AlMe[N(Ph)NN}}\mathrm{(Ph)]_2(3,5\text{-}Me_2py)}$ revealed it to be the first example of a monomeric six-coordinate aluminum alkyl (**III**). In addition, a large *trans* influence was observed for the Al–N distance *trans* to the methyl ligand, the first observation of such an effect for an aluminum complex.



(II)



(III)

Difficulties in preparing $\overline{\mathrm{AlMe[N(Ph)NN}}\mathrm{(Ph)]_2(3,5\text{-}Me_2py)}$ in high yield and the inertness of the methyl ligand to substitution prompted us to investigate alternative routes to mono- and bis(1,3-diphenyltriazenido) complexes of aluminum. In this regard we have investigated the reactivity of 1,3-diphenyltriazene with isobutyl, *tert*-butyl, aryloxide, and Schiff-base aluminum compounds, and the results of this study are presented herein. In addition, the synthesis and spectroscopic and structural characterization of tris(1,3-diaryltriazenido)aluminum complexes, in which the phenyl substituent is monosubstituted at either the 2- or 4-position or pentasubstituted, are reported.

Results and Discussion

Alkylaluminum Triazenide Compounds. Although we have no firm explanation for the mechanism resulting in the exclusive formation of the tris(triazenido)aluminum compound from $\mathrm{AlMe_3}$ (*cf.* eq 1), on the basis of analogy with other group 13 systems, we propose that it involves rapid alkyl–triazenide ligand exchange, e.g., eq 3. If this is indeed true, increased steric bulk of the alkyl substituent should slow one or other (or both) of these ligand-exchange reactions.[9]

$$\mathrm{AlMe_2L} \underset{-\mathrm{AlMe_3}}{\overset{\mathrm{AlMe_2L}}{\rightleftharpoons}} \mathrm{AlMeL_2} \xrightarrow[-\mathrm{AlMe_3}]{\mathrm{AlMe_2L}} \mathrm{AlL_3} \quad (3)$$

Interaction of $\mathrm{AlH(^iBu)_2}$ with 1 or 2 molar equiv of 1,3-diphenyltriazene, at −78 °C, yields $\overline{\mathrm{Al(^iBu)_2[N(Ph)NN}}\mathrm{(Ph)]}$ (**1**) or $\overline{\mathrm{Al(^iBu)[N(Ph)NN}}\mathrm{(Ph)]_2}$ (**2**), respectively (eqs 4 and 5).

$$\mathrm{AlH(^iBu)_2 + (Ph)NNN(H)(Ph)} \xrightarrow[\text{pentane}]{} \underset{\mathbf{1}}{\overline{\mathrm{Al(^iBu)_2[N(Ph)NN}}\mathrm{(Ph)]}} + \mathrm{H_2} \quad (4)$$

$$\mathrm{AlH(^iBu)_2 + 2(Ph)NNN(H)(Ph)} \xrightarrow[\text{hexane/toluene}]{} \underset{\mathbf{2}}{\overline{\mathrm{Al(^iBu)[N(Ph)NN}}\mathrm{(Ph)]_2}} + \mathrm{H_2} + \mathrm{{}^iBuH} \quad (5)$$

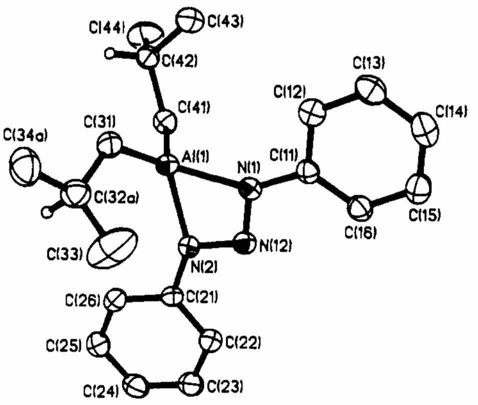


Figure 1. Molecular structure of $\overline{\mathrm{Al(^iBu)_2[N(Ph)NN}}\mathrm{(Ph)]}$ (**1**). Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

Table I. Selected Bond Lengths (Å) and Angles (deg) for $\overline{\mathrm{Al(^iBu)_2[N(Ph)NN}}\mathrm{(Ph)]}$ (**1**)

Al(1)–N(1)	1.971(3)	Al(1)–N(2)	1.962(3)
Al(1)–C(31)	1.956(4)	Al(1)–C(41)	1.952(3)
N(1)–N(12)	1.319(4)	N(1)–C(11)	1.402(4)
N(2)–N(12)	1.321(4)	N(2)–C(21)	1.399(4)
C(31)–C(32a)	1.529(9)	C(31)–C(32b)	1.507(8)
C(32a)–C(33)	1.39(1)	C(32b)–C(33)	1.33(1)
C(32a)–C(34)	1.53(1)	C(32b)–C(34b)	1.55(1)
C(41)–C(42)	1.524(5)	C(42)–C(43)	1.520(6)
C(42)–C(44)	1.521(5)		
N(1)–Al(1)–N(2)	64.7(1)	N(1)–Al(1)–C(31)	115.3(1)
N(1)–Al(1)–C(41)	113.4(1)	N(2)–Al(1)–C(31)	120.9(1)
N(2)–Al(1)–C(41)	108.4(1)	C(31)–Al(1)–C(41)	121.2(1)
Al(1)–N(1)–N(12)	94.5(2)	Al(1)–N(1)–C(11)	147.5(2)
N(12)–N(1)–C(11)	118.0(2)	Al(1)–N(2)–N(12)	94.9(2)
Al(1)–N(2)–C(21)	145.8(2)	N(12)–N(2)–C(21)	118.7(2)
N(1)–N(12)–N(2)	105.8(2)	Al(1)–C(31)–C(32a)	124.9(4)
Al(1)–C(31)–C(32b)	117.6(4)	C(31)–C(32a)–C(33)	117.3(6)
C(31)–C(32b)–C(33)	122.5(7)	C(31)–C(32a)–C(34a)	116.3(8)
C(31)–C(32b)–C(34b)	107.2(6)	C(33)–C(32a)–C(34a)	115.9(8)
C(33)–C(32b)–C(34b)	109.8(7)	Al(1)–C(41)–C(42)	117.9(2)
C(41)–C(42)–C(43)	110.2(3)	C(41)–C(42)–C(44)	111.4(3)
C(43)–C(42)–C(44)	111.2(3)		

Compounds **1** and **2** are both orange-red and soluble in hydrocarbon solvents and have been fully characterized by elemental analysis and IR and NMR spectroscopy (see Experimental Section); in addition, the molecular structure of **1** has been confirmed by X-ray crystallography. Although we have been unable to obtain crystals of **2** suitable for X-ray diffraction studies, the coordination around aluminum is probably similar to that found for other five-coordinate complexes.[10]

The molecular structure of compound **1** is shown in Figure 1; selected bond lengths and angles are given in Table I. Compound **1** is monomeric with no unusual intermolecular contacts. The aluminum atom is four-coordinate distorted tetrahedral, as a consequence of the small bite angle of the triazenide ligand, i.e., N(1)–Al(1)–N(2) = 64.7(1)°. The ligation of the triazenide is essentially identical to that observed for the six-coordinate compounds $\overline{\mathrm{Al[N(Ph)NN}}\mathrm{(Ph)]_3}$[6] and $\overline{\mathrm{AlMe[N(Ph)NN}}\mathrm{(Ph)_2(3,5\text{-}Me_2Py)}$,[8] indicating the ligand geometry to be relatively insensitive to the coordination environment around aluminum.

Reaction of $\mathrm{Al(^tBu)_3}$[11] with 1 equiv of 1,3-diphenyltriazene at −78 °C allows for the isolation of the mono(triazenido) compound

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[8] Leman, J. T.; Barron, A. R. *Organometallics* **1989**, *8*, 1828.

[9] For an example of the control exerted on ligand-exchange equilibria by the steric bulk of an alkyl substituent see: Shreve, A. P.; Mullhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409.

[10] See for example: Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1987**, *109*, 6852.

[11] Uhl, W. *Z. Anorg. Allg. Chem.* **1989**, *570*, 37.

$Al(^tBu)_2[N(Ph)NN(Ph)]$ (**3**). On the basis of spectroscopic characterization, compound **3** has a structure analogous to **1**; however, unlike **2**, compound **3** does not react with further equivalents of 1,3-diphenyltriazene.

While compounds **1** and **3** are indefinitely stable under an inert atmosphere in both the solid state and solution, compound **2** undergoes ligand exchange, at ambient temperatures (eq 6). These observations are consistent with the inhibition of the alkyl–triazenide exchange with increasing steric bulk of the aluminum alkyl.

$$2Al(^iBu)[N(Ph)NHN(Ph)]_2 \xrightarrow{\text{room temp}} Al(^iBu)_2[N(Ph)NN(Ph)] + Al[N(Ph)NN(Ph)]_3 \quad (6)$$

Aluminum Aryloxide Triazenide Compounds. The reaction of $AlMe_2(BHT)(OEt_2)$[12] with 1 molar equiv of 1,3-diphenyltriazene yields the mixed alkyl–aryloxide–triazenide compound **4** in moderate yield (eq 7). By contrast, the reaction of $AlH_2(BHT)(NMe_3)$[13] with (Ph)NNN(H)(Ph) results in the formation of $Al(BHT)[N(Ph)NN(Ph)]_2$ (**5**), in good yield (eq 8). Compound **5** slowly (days at 25 °C in toluene solution) undergoes ligand exchange, in a manner analogous to that observed for compound **2**, to yield $Al[N(Ph)NN(Ph)]_3$ and $Al(BHT)_2[N(Ph)NN(Ph)]$ (**6**) (eq 9). Compound **6** may also be prepared directly from the reaction of $AlMe(BHT)_2$[14] with 1 equiv of 1,3-diphenyltriazene, i.e., eq 10. Compounds **4**–**6** are all orange and soluble in hydrocarbon solvents. Elemental analysis and IR and NMR spectroscopy (see Experimental Section) are consistent with their formulation as given. The molecular structure of **6** has been determined by X-ray crystallography.

$$AlMe_2(BHT)(OEt_2) + (Ph)NNN(H)(Ph) \longrightarrow \underset{\mathbf{4}}{AlMe(BHT)[N(Ph)NN(Ph)]} + MeH \quad (7)$$

$$AlH_2(BHT)(NMe_3) + 2(Ph)NNN(H)(Ph) \longrightarrow \underset{\mathbf{5}}{Al(BHT)[N(Ph)NN(Ph)]_2} + 2H_2 + NMe_3 \quad (8)$$

$$2Al(BHT)[N(Ph)NN(Ph)]_2 \longrightarrow Al[N(Ph)NN(Ph)]_3 + \underset{\mathbf{6}}{Al(BHT)_2[N(Ph)NN(Ph)]} \quad (9)$$

$$AlMe(BHT)_2 + (Ph)NNN(H)(Ph) \longrightarrow Al(BHT)_2[N(Ph)NN(Ph)] + MeH \quad (10)$$

The structure of compound **6** is shown in Figure 2; selected bond lengths and angles are given in Table II. The compound contains a crystallographically-imposed C_2 axis coincident with the Al(1)–N(2) vector. The aryloxide ligands adopt a propeller-like conformation. As was observed for compound **1**, the aluminum atom in **6** is in a highly distorted tetrahedral environment, with the smallest angle being associated with the triazenide chelate [N(1)–Al(1)–N(1a) = 64.7(1)°]. Given the difference in steric bulk of the BHT and isobutyl ligands, it is interesting to note that the geometry around aluminum in **6** is surprisingly similar to that in **1**. The O(1)–Al(1)–O(1a) angle in **6** [124.5(2)°] is only slightly larger than the equivalent C(31)–Al(1)–C(41) angle in **1** [121.2(2)°]. Furthermore, the extents by which the AlX_2 [X = C (**1**), O (**6**)] plane is twisted away from the perpendicular to the plane defined by the triazenide nitrogens and the aluminum atom are comparable [7.6° (**1**), 8.4° (**6**)].

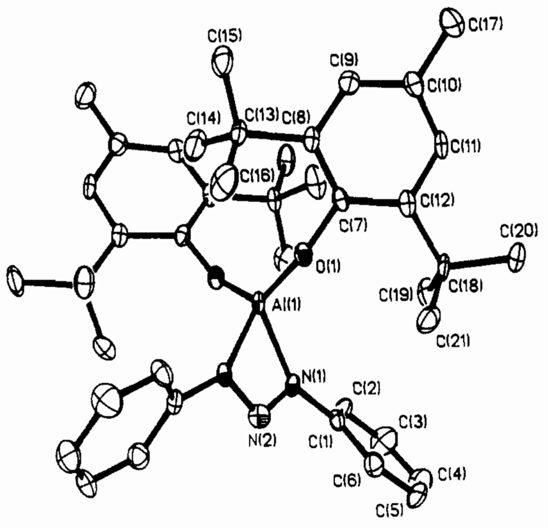

Figure 2. Molecular structure of $Al(BHT)_2[N(Ph)NN(Ph)]$ (**6**). Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

Table II. Selected Bond Lengths (Å) and Angles (deg) for $Al(BHT)_2[N(Ph)NN(Ph)]$ (**6**)

Al(1)–N(1)	1.958(3)	Al(1)–O(1)	1.689(3)
N(1)–N(2)	1.303(4)	N(1)–C(1)	1.426(5)
O(1)–C(7)	1.372(4)		
N(1)–Al(1)–N(1a)	65.3(2)	N(1)–Al(1)–O(1)	117.5(1)
N(1)–Al(1)–O(1a)	108.8(1)	O(1)–Al(1)–O(1a)	124.5(2)
Al(1)–N(1)–N(2)	93.1(2)	Al(1)–N(1)–C(1)	149.7(3)
N(2)–N(1)–C(1)	116.1(3)	N(1)–N(2)–N(1a)	108.4(4)
Al(1)–O(1)–C(7)	151.5(2)		

Aluminum Schiff-Base Triazenide Compounds. The reaction of compound **1** with *N,N'*-ethylenebis(salicylideneamine) does not result in the substitution of both isobutyl groups but rather results in the liberation of 1 equiv of alkane and the protonated triazenide ligand (eq 11).[15] On the basis of its ^1H NMR spectrum (see Experimental Section), compound **7** appears to be essentially the same in structure as the ethyl[16] and methyl[17] analogs, whose structures have been determined by X-ray crystallography (see below), the aluminum being five-coordinate.

$$Al(^iBu)_2[N(Ph)NN(Ph)] + H_2salen \longrightarrow \underset{\mathbf{7}}{Al(^iBu)(salen)} + (Ph)NNN(H)(Ph) + {}^iBuH \quad (11)$$

We have previously shown[17] that AlMe(salen) reacts with a variety of protic acids, HX, to yield the corresponding complexes, eq 12. Treatment of AlMe(salen) with HN(Ph)NN(Ph) allows the isolation of Al[N(Ph)NN(Ph)](salen) **8**; *cf.* eq 13. Unfortunately, we have been unable to obtain crystals of **8** suitable for

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(12) Power, M. B.; Healy, M. D.; Barron, A. J. *J. Coord. Chem.* **1990**, *21*, 363.

(13) Healy, M. D.; Gravelle, P.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1993**, 441.

(14) Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2563.

(15) We have previously observed a lack of reactivity for aluminum alkyls in dialkylaluminum amide compounds: Healy, M. D.; Leman, J. T.; Barron, A. R. *J. Am. Chem. Soc.* **1991**, *113*, 2776.

(16) Dzugan, S. J.; Goedken, V. L. *Inorg. Chem.* **1986**, *25*, 2858.

(17) Gurian, P. L.; Cheatham, L. K.; Ziller, J. W.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1991**, 1449.

$$\mathrm{AlMe(salen) + HX \rightarrow AlX(salen) + MeH} \qquad (12)$$

$$\mathrm{X = OH, OR, O_2CR}$$

X-ray diffraction; however, the IR spectrum contains bands at 1279, 1303, and 1330 cm^{-1} which are characteristic of chelating triazenide groups.[6] The peak position (δ 11) and line width ($W_{1/2}$ = 940 Hz) of the single peak observed in the ^{27}Al NMR spectrum of compound **8** are consistent with those of a highly distorted octahedral site. The spectroscopic data are therefore consistent with a structure analogous to that found for M(acac)(salen) (Hacac = acetylacetone; M = Al, Co),[17,18] in which the metals are in a distorted octahedral environment and the acac group acts as a chelate ligand.

During the course of this study, we obtained crystals of AlMe(salen) suitable for X-ray analysis, where our previous attempts had been frustrated by crystal twinning.[17] The molecular structure of AlMe(salen) is shown in Figure 3; selected bond lengths and angles are given in Table III.

Tris(diaryltriazenido) Compounds of Aluminum. All the triazenido compounds of the group 13 metals prepared in our laboratory have been derived from 1,3-diphenyltriazene (**I**). In order to probe possible structural and spectroscopic changes upon substitution of the aryl ring, we have now prepared a homologous series of tris(diaryltriazenido) compounds $\overline{\mathrm{Al[N(Ar)NN}}\mathrm{(Ar')]_3}$. Furthermore, we have prepared the tris(triazenido) complex derived from the asymmetric triazene (Ph)NNN(H)(4-MeOPh).[19] All the substituted triazenido compounds are prepared in a manner analogous to that for the parent compound, eq 13.

$$\mathrm{AlR_3 + 3(Ar)NNN(H)(Ar') \longrightarrow \overline{Al[N(Ar)NN}(Ar')]_3 + 3RH} \qquad (13)$$

Ar = Ar′ = 2-MePh (**9**), 4-MePh (**10**),
4-MeOPh (**11**), 4-FPh (**12**), 4-ClPh (**13**),
4-BrPh (**14**), C_6F_5 (**15**); Ar = Ph, Ar′ = 4-MeOPh (**16**)

Compounds **9**–**16** have been characterized by spectral data (see Experimental Section. The ^{27}Al NMR spectra consist of broad resonances whose shifts (δ 24–34 ppm), while indicative of six-coordinate aluminum centers, are uncharacteristically broad ($W_{1/2}$ = 1400–2460 Hz).[20] This broadening is possibly due to the high trigonal distortion observed in the solid state (*vide infra*) but may also be exacerbated by coupling to the quadrupolar ^{14}N nuclei. However, another effect may be operating in view of the ^{27}Al NMR spectrum obtained for the perfluorinated compound (**15**), for which the line width ($W_{1/2}$ = 625 Hz), although still broad with respect to six-coordinate species commonly observed, is a notable exception to the large line widths in the ^{27}Al NMR spectra for the other tris(triazenido) complexes. The smaller line width for compound **15** may be rationalized from the perspective of a decrease in the intermolecular interactions due to the fluorocarbon periphery of the molecule, and the subsequent decrease in spin–spin exchange collisions, which in turn results in an increase of the transverse relaxation time (T_2) and a decrease in the line width.[21] It is therefore reasonable to expect that the increased line widths for compounds **9**–**14** and **16** as compared to **15** are due to efficient intermolecular interactions in solution. The IR spectra of **9**–**16** show bands at 1303–1324, 1276–1306, and 1247–1293 cm^{-1}, which are characteristic of chelating triazenide groups. The chelating coordination mode has been confirmed for **9**, **11**, and **13** by X-ray crystallography.

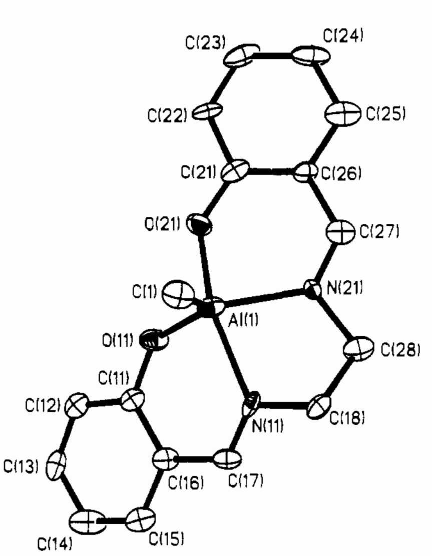
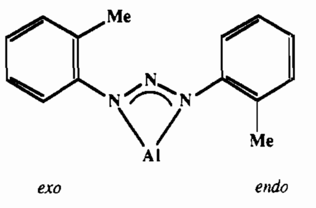


Figure 3. Molecular structure of AlMe(salen). Thermal ellipsoids are drawn at the 30% level, and hydrogen atoms are omitted for clarity.

The molecular structures of **9**, **11**, and **13** are shown in Figures 4–6, respectively; selected bond lengths and angles are given in Tables IV–VI. The aluminum in each compound is in a trigonally distorted octahedral coordination environment, with the *trans* N–Al(1)–N angles in the range 153.8(2)–163.2(4)°. The triazenido ligands are arranged in a pseudo-C_3 propeller arrangement. The Al–N [1.968(4)–2.003(9) Å] and N–N [1.30(1)–1.33(1) Å] distances and the N–N–N [105.1(9)–106.5(8)°] and Al–N–C [145.1(8)–150.3(7)°] angles for all the compounds appear to be essentially independent of the substituents on the triazenide ligand.

Whereas the aryl rings in **11** and **13** are nearly coplanar with the triazenide nitrogens, those in **9** are significantly twisted away from coplanarity due to the steric influence of the ortho methyl groups. It is worth noting that in the solid state the *o*-tolyl groups adopt one of two conformations which may be termed *exo* and *endo*, for those situated away from or toward the aluminum, respectively (**IV**). In the solid-state structure of **9**, each ligand has one methyl group *exo* and one *endo*. This is in contrast to the uncomplexed ligand (see below), where both the methyl groups occupy *endo* orientations. This difference in ligand orientation is clearly due to the steric hindrance in compound **9** *versus* the free ligand. The positions of the methyl groups in the *o*-tolyl groups associated with N(4) and N(5) are such that they are placed above and below the aluminum atom (see Figure 4). However, the intramolecular (observed) C···Al and (calculated)



(IV)

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(18) Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Chem. Commun.* **1969**, 1248.

(19) It should be noted that (Ph)NNN(H)(4-MeOPh) is one of a prototropic, tautomeric pair, written in this fashion for convenience, e.g., (Ph)NNN(H)(4-MeOPh) ↔ (Ph)N(H)NN(4-MeOPh). Neither can be isolated in pure form.

(20) Due to the high symmetry of the octahedral environment, the ^{27}Al NMR signals for $\mathrm{AlL_6}$ complexes tend to be narrow ($W_{1/2}$ = 3–70 Hz): Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: London, 1978.

(21) Roberts, J. D. *Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959.

Table III. Selected Bond Lengths (Å) and Angles (deg) for AlMe(salen)

Al(1)–C(1)	1.95(1)	Al(1)–O(11)	1.794(7)
Al(1)–O(21)	1.823(7)	Al(1)–N(11)	2.041(8)
Al(1)–N(21)	2.033(8)	O(11)–C(11)	1.32(1)
O(21)–C(21)	1.30(1)	N(11)–C(17)	1.28(1)
N(11)–C(18)	1.46(1)	N(21)–C(27)	1.28(1)
N(21)–C(28)	1.47(1)		
C(1)–Al(1)–O(11)	117.6(4)	C(1)–Al(1)–O(21)	103.9(4)
O(11)–Al(1)–O(21)	89.0(3)	C(1)–Al(1)–N(11)	97.8(4)
O(11)–Al(1)–N(11)	88.0(3)	O(21)–Al(1)–N(11)	156.9(3)
C(1)–Al(1)–N(21)	108.5(4)	O(11)–Al(1)–N(21)	133.1(3)
O(21)–Al(1)–N(21)	87.8(3)	N(11)–Al(1)–N(21)	77.7(3)
Al(1)–O(11)–C(11)	133.6(6)	Al(1)–O(21)–C(21)	133.8(6)
Al(1)–N(11)–C(17)	128.6(7)	Al(1)–N(11)–C(18)	112.3(5)
C(17)–N(11)–C(18)	119.0(8)	Al(1)–N(21)–C(27)	126.7(7)
Al(1)–N(21)–C(28)	116.3(5)		

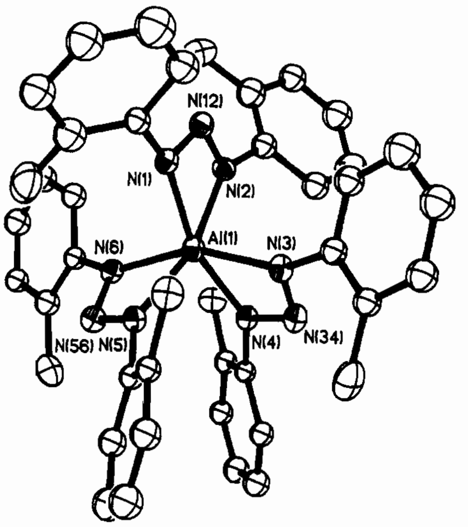


Figure 4. Molecular structure of $\overline{\mathrm{Al[N(2\text{-}MePh)NN}}\mathrm{(2\text{-}MePh)]_3}$ (**9**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and the labels for the phenyl carbon atoms are omitted for clarity.

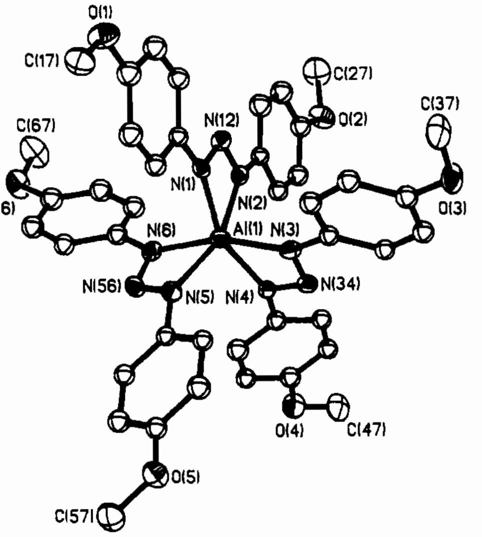


Figure 5. Molecular structure of $\overline{\mathrm{Al[N(4\text{-}MeOPh)NN}}\mathrm{(4\text{-}MeOPh)]_3}$ (**11**). Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms and the labels for phenyl carbon atoms are omitted for clarity.

H···Al distances are sufficiently large to preclude the possibility of any agostic C–H–Al interaction.[22]

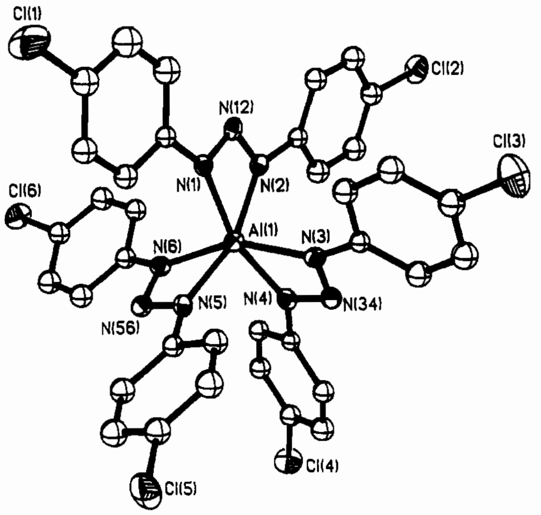
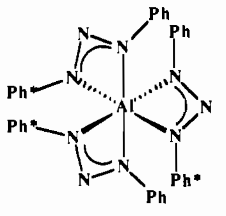


Figure 6. Molecular structure of $\overline{\mathrm{Al[N(4\text{-}ClPh)NN}}\mathrm{(4\text{-}ClPh)]_3}$ (**13**). Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms and the labels for the phenyl carbon atoms are omitted for clarity.

It is clear from the spectroscopy of **9–16** and the molecular structures of **9**, **11**, and **13** that substitution of the aryl ring does not appreciably alter the structure of the tris(triazenido)aluminum complex.

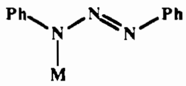
Coordination compounds in which the central atom is bound to three unsymmetrical bidentate ligands may exist in two geometrically isomeric forms, facial (*cis*) and meridional (*trans*). While we have been unable to grow crystals of $\overline{\mathrm{Al[N(Ph)NN}}\mathrm{(4\text{-}MeOPh)]_3}$ (**16**) suitable for X-ray diffraction, the ^{1}H and ^{13}C NMR spectra are consistent with the presence of a single meridional isomer (V).[23] This is analogous to the results reported for aluminum tris(benzoylacetonate).[24] Failure to obtain any of the facial isomer for $\overline{\mathrm{Al[N(Ph)NN}}\mathrm{(4\text{-}MeOPh)]_3}$ is undoubtedly reflects the lability of the complex and the greater stability of the *trans* isomer.[24,25]



Ph* = 4-MeOPh

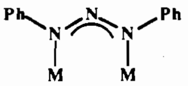
(V)

Are Aluminum Triazenide Compounds Structural Analogs of Aluminum Carboxylates? The 1,3-diphenyltriazenide anion, [PhN=N—NPh]$^-$, has been reported to act as a monodentate (VI), chelating (VII), or bridging (VIII) ligand toward transition metals,[26] suggesting a formal analogy to the carboxylate anion, [O=C(R)—O]$^-$; both ligands are monovalent, hard donors and



(VI)

(VII)



(VIII)

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[22] It should be noted that we have previously observed the presence of an agostic C–H–In interaction for the ortho methyl groups in In(2,4,6-$Me_3C_6H_2$)$_3$: Leman, J. T.; Barron, A. R. *Organometallics* **1989**, *8*, 2214.

[23] It is interesting to note that while the ^{1}H NMR shows inequivalent OCH_3 groups (ratio 2:1), the ^{13}C NMR spectrum shows only inequivalent aromatic rings. Furthermore, no evidence for the facial isomer is found.

[24] Fay, R. C.; Piper, T. S. *J. Am. Chem. Soc.* **1962**, *84*, 2303.

[25] For a detailed study of the ligand-exchange reactions observed for Al(β-diketonate)$_3$, see: Saito, K.; Nagasawa, A. *Polyhedron* **1990**, *9*, 215.

[26] Moore, D. S.; Robinson, S. D. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 1.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for Al[N(2-MePh)NN(2-MePh)]$_3$·(C$_7$H$_8$) (**9**)

Al(1)–N(1)	1.98(1)	Al(1)–N(2)	1.981(9)
Al(1)–N(3)	1.977(8)	Al(1)–N(4)	1.979(9)
Al(1)–N(5)	2.000(9)	Al(1)–N(6)	1.970(8)
N(1)–N(12)	1.33(1)	N(1)–C(11)	1.44(1)
N(12)–N(2)	1.32(1)	N(2)–C(21)	1.46(1)
N(3)–N(34)	1.31(1)	N(3)–C(31)	1.42(1)
N(34)–N(4)	1.33(1)	N(4)–C(41)	1.42(1)
N(5)–N(56)	1.31(1)	N(5)–C(51)	1.40(1)
N(56)–N(6)	1.32(1)	N(6)–C(61)	1.41(1)

N(1)–Al(1)–N(2)	64.5(4)	N(1)–Al(1)–N(3)	101.4(4)
N(2)–Al(1)–N(3)	95.5(4)	N(1)–Al(1)–N(4)	160.9(4)
N(2)–Al(1)–N(4)	103.1(4)	N(3)–Al(1)–N(4)	64.1(4)
N(1)–Al(1)–N(5)	104.2(4)	N(2)–Al(1)–N(5)	163.2(4)
N(3)–Al(1)–N(5)	99.1(4)	N(4)–Al(1)–N(5)	90.8(4)
N(1)–Al(1)–N(6)	100.8(4)	N(2)–Al(1)–N(6)	104.4(4)
N(3)–Al(1)–N(6)	155.0(4)	N(4)–Al(1)–N(6)	96.3(4)
N(5)–Al(1)–N(6)	64.1(4)	Al(1)–N(1)–N(12)	94.9(7)
Al(1)–N(1)–C(11)	149.6(8)	N(12)–N(1)–C(11)	114.3(9)
N(1)–N(12)–N(2)	105.1(9)	Al(1)–N(2)–N(12)	95.3(6)
Al(1)–N(2)–C(21)	145.1(8)	N(12)–N(2)–C(21)	118.5(9)
Al(1)–N(3)–N(34)	95.5(6)	Al(1)–N(3)–C(31)	148.5(8)
N(34)–N(3)–C(31)	115.9(8)	N(3)–N(34)–N(4)	105.3(8)
Al(1)–N(4)–N(34)	94.7(6)	Al(1)–N(4)–C(41)	145.3(7)
N(34)–N(4)–C(41)	115.7(8)	Al(1)–N(5)–N(56)	93.9(6)
Al(1)–N(5)–C(51)	145.8(7)	N(56)–N(5)–C(51)	116.5(8)
N(5)–N(56)–N(6)	106.5(8)	Al(1)–N(6)–N(56)	95.0(6)
Al(1)–N(6)–C(61)	146.4(8)	N(56)–N(6)–C(61)	118.6(9)

Table V. Selected Bond Lengths (Å) and Angles (deg) for Al[N(4-MeOPh)NN(4-MeOPh)]$_3$ (**11**)

Al(1)–N(1)	1.989(8)	Al(1)–N(2)	1.990(8)
Al(1)–N(3)	1.977(8)	Al(1)–N(4)	1.996(8)
Al(1)–N(5)	2.003(9)	Al(1)–N(6)	1.974(8)
N(1)–N(12)	1.32(1)	N(1)–C(11)	1.41(1)
N(12)–N(2)	1.32(1)	N(2)–C(21)	1.41(1)
N(3)–N(34)	1.32(1)	N(3)–C(31)	1.41(1)
N(34)–N(4)	1.34(1)	N(4)–C(41)	1.39(1)
N(5)–N(56)	1.30(1)	N(5)–C(51)	1.42(1)
N(56)–N(6)	1.32(1)	N(6)–C(61)	1.39(1)

N(1)–Al(1)–N(2)	64.1(3)	N(1)–Al(1)–N(3)	98.4(3)
N(2)–Al(1)–N(3)	97.0(3)	N(1)–Al(1)–N(4)	155.7(4)
N(2)–Al(1)–N(4)	99.3(3)	N(3)–Al(1)–N(4)	64.5(3)
N(1)–Al(1)–N(5)	103.9(3)	N(2)–Al(1)–N(5)	158.0(4)
N(3)–Al(1)–N(5)	103.3(3)	N(4)–Al(1)–N(5)	97.2(3)
N(1)–Al(1)–N(6)	96.9(3)	N(2)–Al(1)–N(6)	98.2(3)
N(3)–Al(1)–N(6)	162.0(4)	N(4)–Al(1)–N(6)	103.4(3)
N(5)–Al(1)–N(6)	63.7(3)	Al(1)–N(1)–N(12)	95.0(6)
Al(1)–N(1)–C(11)	149.8(6)	N(12)–N(1)–C(11)	115.2(8)
N(1)–N(12)–N(2)	106.0(7)	Al(1)–N(2)–N(12)	94.8(6)
Al(1)–N(2)–C(21)	147.8(7)	N(12)–N(2)–C(21)	117.3(8)
Al(1)–N(3)–N(34)	95.7(6)	Al(1)–N(3)–C(31)	147.7(7)
N(34)–N(3)–C(31)	116.5(8)	N(3)–N(34)–N(4)	105.5(7)
Al(1)–N(4)–N(34)	94.2(5)	Al(1)–N(4)–C(41)	150.3(7)
N(34)–N(4)–C(41)	115.2(8)	Al(1)–N(5)–N(56)	94.7(6)
Al(1)–N(5)–C(51)	146.8(7)	N(56)–N(5)–C(51)	117.0(8)
N(5)–N(56)–N(6)	106.3(7)	Al(1)–N(6)–N(56)	95.3(5)
Al(1)–N(6)–C(61)	147.3(7)	N(56)–N(6)–C(61)	116.3(8)

form a four-center metallacycle as a chelating ligand and a three-center bridge between two metal centers. However, with respect to aluminum, does the analogy between carboxylate and triazenide hold?

Table VI. Selected Bond Lengths (Å) and Angles (deg) for Al[N(4-ClPh)NN(4-ClPh)]$_3$ (**13**)

Al(1)–N(1)	1.968(4)	Al(1)–N(2)	1.985(4)
Al(1)–N(3)	1.993(4)	Al(1)–N(4)	1.968(4)
Al(1)–N(5)	1.987(4)	Al(1)–N(6)	1.979(4)
N(1)–N(12)	1.320(5)	N(1)–C(11)	1.404(6)
N(12)–N(2)	1.309(5)	N(2)–C(21)	1.417(6)
N(3)–N(34)	1.313(5)	N(3)–C(31)	1.412(6)
N(34)–N(4)	1.315(5)	N(4)–C(41)	1.405(6)
N(5)–N(56)	1.322(5)	N(5)–C(51)	1.403(6)
N(56)–N(6)	1.316(5)	N(6)–C(61)	1.407(6)

N(1)–Al(1)–N(2)	64.1(2)	N(1)–Al(1)–N(3)	103.1(2)
N(2)–Al(1)–N(3)	94.9(2)	N(1)–Al(1)–N(4)	161.4(2)
N(2)–Al(1)–N(4)	102.3(2)	N(3)–Al(1)–N(4)	63.9(2)
N(1)–Al(1)–N(5)	100.2(2)	N(2)–Al(1)–N(5)	161.5(2)
N(3)–Al(1)–N(5)	98.5(2)	N(4)–Al(1)–N(5)	95.1(2)
N(1)–Al(1)–N(6)	99.2(2)	N(2)–Al(1)–N(6)	107.2(2)
N(3)–Al(1)–N(6)	153.8(2)	N(4)–Al(1)–N(6)	97.0(2)
N(5)–Al(1)–N(6)	63.8(2)	Al(1)–N(1)–N(12)	95.2(3)
Al(1)–N(1)–C(11)	147.0(3)	N(12)–N(1)–C(11)	117.9(4)
N(1)–N(12)–N(2)	105.9(3)	Al(1)–N(2)–N(12)	94.7(3)
Al(1)–N(2)–C(21)	146.9(3)	N(12)–N(2)–C(21)	116.6(4)
Al(1)–N(3)–N(34)	94.6(3)	Al(1)–N(3)–C(31)	148.1(3)
N(34)–N(3)–C(31)	117.2(4)	N(3)–N(34)–N(4)	105.8(3)
Al(1)–N(4)–N(34)	95.7(3)	Al(1)–N(4)–C(41)	145.6(3)
N(34)–N(4)–C(41)	117.7(4)	Al(1)–N(5)–N(56)	95.2(3)
Al(1)–N(5)–C(51)	147.4(3)	N(56)–N(5)–C(51)	117.3(4)
N(5)–N(56)–N(6)	105.2(3)	Al(1)–N(6)–N(56)	95.8(3)
Al(1)–N(6)–C(61)	147.2(3)	N(56)–N(6)–C(61)	117.0(4)

In all of the triazenido compounds of aluminum we have isolated at this time, the triazenide ligands bind exclusively in a bidentate chelate manner. By contrast, no such coordination has been crystallographically characterized for aluminum carboxylates. Instead, where structural elucidations have been performed, the carboxylate adopts a monodentate[27] or bridging coordination.[28] In fact for each of the classes of triazenide compounds structurally characterized for aluminum, there is a β-diketonate analog but not one of a carboxylate. For example, in AlL(salen), for L = carboxylate, the aluminum is five-coordinate, with a monodentate carboxylate, while, for L = N(Ph)NN(Ph) or acac, the aluminum is six-coordinate with a chelating ligand. Thus, 1,3-diaryltriazenide could be better considered to be an analog of the β-diketonate anion [OC(R)CH(O)CR]$^-$.

Given the isoelectronic nature and structural similarities of the triazenide and carboxylate anions, why is the chelating mode of coordination for the latter unfavorable? One reason that must clearly be considered in that greater steric strain would be imposed on a chelating carboxylate than is observed for the triazenide. Upon coordination to aluminum, the N–N–N angle in a triazene ligand is reduced from *ca.* 112° to *ca.* 106°, a change of –6°. From the similarity in Al–O *versus* Al–N and N$\underset{\cdots}{-}$N *versus* C$\underset{\cdots}{-}$O bond distances, a similar chelate geometry would be expected for both the carboxylate and triazenide. However, the O–C–O bond angle in a free acid is *ca.* 123°. Thus, upon coordination, the O–C–O angle would be reduced by *ca.* 18°, imposing significant ring strain in the AlOCO cycle.

In summary, the 1,3-diaryltriazenide ligand is best likened chemically to a β-diketonate ligand, but with a small "bite angle", 63–65° *versus* 80–90° for β-diketonates.

Molecular Structures of (C$_6$F$_5$)NNN(H)(C$_6$F$_5$) and (2-MePh)NNN(H)(2-MePh)·(2-MePh)NH$_2$. The free triazenes are generally believed to adopt a *trans* configuration (**I**), and this arrangement has been confirmed for (Ph)NNN(H)(Ph)[29] and a number of para-substituted derivatives.[30,31] Two structural forms have been observed; an α-modification consisting of H-bonded dimeric complexes and a β-modification formed by infinite, helical chains of H-bonded molecules. The majority of structures have been the β-modification. In both crystallographic forms, the phenyl rings are found to be coplanar with the triazene's N$_3$ plane. However, no structural data are available on ortho-substituted triazenes. In order to determine the effects of ortho

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(27) Atwood, J. L.; Hunter, W. E.; Crissinger, *J. Organomet. Chem.* **1977**, 4127, 403.

(28) Sobota, P.; Mustafa, M. O.; Ukko, J.; Lis, T., *J. Chem. Soc., Dalton Trans.* **1990**, 1809.

(29) Gladkova, V. F.; Kondrashev, Yu. D. *Kristallografiya* **1972**, *17*, 33.

(30) Kondrashev, Yu. D. *Kristallografiya* **1968**, *13*, 622.

(31) Omel'chenko, Yu. A.; Kondrashev, Yu. D. *Kristallografiya* **1972**, *17*, 947.

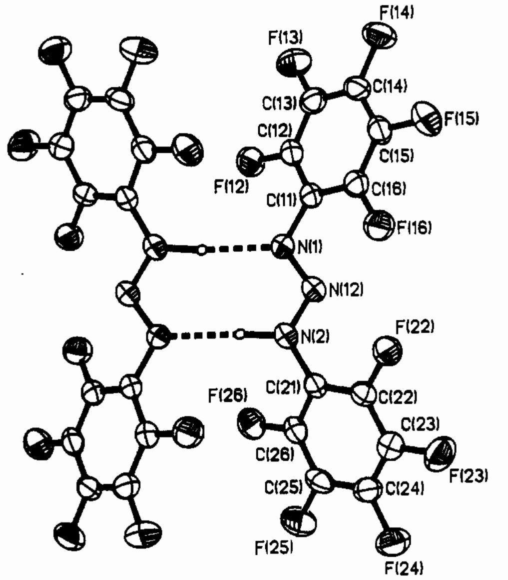

Figure 7. Structure of the hydrogen-bonded dimer of $(C_6F_5)NNN(H)(C_6F_5)$.

Table VII. Selected Bond Lengths (Å) and Angles (deg) for $(C_6F_5)NNN(H)(C_6F_5)$

N(1)–N(12)	1.286(3)	N(1)–C(11)	1.413(3)
N(2)–N(12)	1.315(3)	N(2)–C(21)	1.400(3)
N(2)–H(2)	1.094[a]	H(2)···N(1a)	1.999[a]
N(12)–N(1)–C(11)	113.8(2)	N(12)–N(2)–C(21)	117.7(2)
N(12)–N(2)–H(2)	115.9[a]	C(21)–N(2)–H(2)	119.5[a]
N(1)–N(12)–N(2)	112.8(2)	N(2)–H(2)–N(1a)	176.9[a]

[a] No esd's given for bond lengths and angles associated with the hydrogen; see Experimental Section.

substitution on the molecular planarity and H-bonded supramolecular structure, we have determined the molecular structure of $(C_6F_5)NNN(H)(C_6F_5)$.

The hydrogen-bridged dimeric α-structure of $(C_6F_5)NNN(H)(C_6F_5)$ is shown in Figure 7; selected bond lengths and angles are given in Table VII. As was found previously,[29-31] there is a significant nonequivalence of the N–N distances, consistent with the localization of the double bond between N(1) and N(2). This resonance form is further confirmed by the position of the hydrogen atom, which was located and refined. Unlike previous structures, that of $(C_6F_5)NNN(H)(C_6F_5)$ is nonplanar, the aryl rings being twisted *ca.* 40° out of the N–N–N plane. This distortion is a consequence of steric interactions between the fluoro substituents on adjacent triazene molecules in the hydrogen-bridged dimeric units (*cf.* Figure 7). No evidence was found for the existence of a helical β-modification of $(C_6F_5)NNN(H)(C_6F_5)$.

The synthesis of (2-MePh)NNN(H)(2-MePh) involves the diazotization and coupling of 2-methylaniline (see Experimental Section). However, unlike the para-substituted derivatives, which form hydrogen-bonded dimers, (2-MePh)NNN(H)(2-MePh) crystallizes from hexane with 1 molar equiv of $(2\text{-MePh})NH_2$. The presence in the ^1H NMR of the crystals of two distinct peaks due to the triazene (δ 9.53) and the aniline (δ 3.54) disallows the formation of a triazenide salt, i.e., $[(2\text{-MePh})NH_3][(2\text{-MePh})NNN(2\text{-MePh})]$. However, the IR spectrum shows the presence of hydrogen-bonding, which is confirmed by X-ray crystallography.

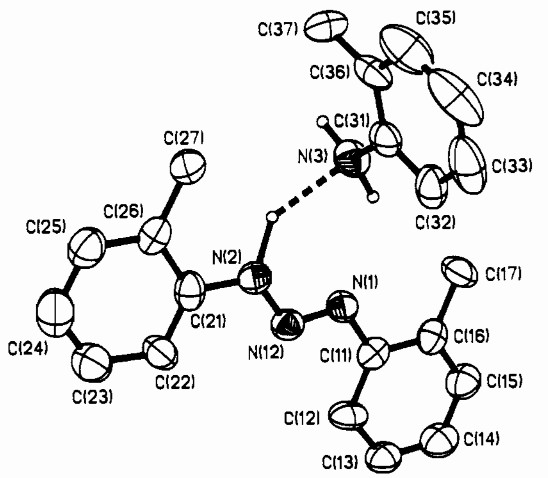

Figure 8. Structure of the hydrogen-bonded complex $(2\text{-MePh})NNN(H)(2\text{-MePh})\cdot(2\text{-MePh})NH_2$.

Table VIII. Selected Bond Lengths (Å) and Angles (deg) for $(2\text{-MePh})NNN(H)(2\text{-MePh})\cdot(2\text{-MePh})NH_2$

N(1)–N(12)	1.259(8)	N(1)–C(11)	1.432(6)
N(2)–N(12)	1.355(6)	N(2)–C(21)	1.401(8)
N(2)–H(2)	1.361[a]	N(3)–C(31)	1.394(9)
N(3)–H(3a)	1.072[a]	N(3)–H(3b)	1.071[a]
N(3)···H(2)	2.031[a]		
N(12)–N(1)–C(11)	113.2(4)	N(12)–N(2)–C(21)	118.6(4)
N(12)–N(2)–H(2)	112.3[a]	C(21)–N(2)–H(2)	120.6[a]
N(1)–N(12)–N(2)	112.8(4)	C(31)–N(3)–H(3)	126.2[a]

[a] No esd's given for bond lengths and angles associated with the hydrogens; see Experimental Section.

The structure of $(2\text{-MePh})NNN(H)(2\text{-MePh})\cdot(2\text{-MePh})NH_2$ is shown in Figure 8; selected bond lengths and angles are given in Table VIII. The ortho methyl groups of the triazene are both in a pseudo-*endo* orientation (see above). Such a configuration would preclude the formation of a triazene hydrogen-bonded dimer as seen in the β-modification of (Ar)NNN(H)(Ar).[29-31] Instead, the triazene is complexed with the aniline via a single hydrogen bond. While the N(3)···H(2) distance (2.031 Å) is comparable to that in (Ar)NNN(H)(Ar) (see above and refs. 29–31), the N(2)–H(2) σ-bonded distances (1.361 Å) is significantly lengthened compared to that expected for a N–H bond (0.9–1.1 Å). This lengthening would suggest a strong hydrogen-bonded interaction; however, it is interesting to note that the distortion from planarity of N(3) is small, *ca.* 6°. As observed in the structure of $(C_6F_5)NNN(H)(C_6F_5)$, there is a distinct inequality in the N–N bond distance. In fact, the difference, Δ(N–N), in $(C_6F_5)NNN(H)(C_6F_5)$ (0.029 Å) is smaller than that in (2-MePh)NNN(H)(2-MePh) (0.057 Å), suggesting that the presence of mutual hydrogen-bonding in the former has the effect of delocalization of the N—N=N resonance structure.

Experimental Section

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Melting points were determined in sealed capillaries and are uncorrected. IR spectra (4000–400 cm^{-1}) were recorded on a Nicolet 5ZDX FT-IR spectrometer in Nujol mulls or KBr pellets. NMR spectra were recorded on Bruker AM-250 (^1H), AM-500 (^{13}C) and WM-300 (^{27}Al, ^{19}F) spectrometers [δ in ppm relative to external $SiMe_4$ (^1H and ^{13}C), external $[Al(H_2O_6]^{3+}$ (^{27}Al), and external $CFCl_3$ (^{19}F)]. Mass spectra were recorded using a JEOL AX-505H mass spectrometer and associated data system. All manipulations were carried out under nitrogen. Solvents were dried, distilled, and degassed before use. $AlH(^iBu)_2$ was used as received from commercial sources. $Al(^tBu)_3$,[11] $AlMe_2(BHT)(OEt_2)$,[12] $AlH_2(BHT)(NMe_3)$,[13] $AlMe(BHT)_2$,[14] AlMe(salen),[17] (Ph)NNN(H)(Ph),[32] and $C_6F_5NH_2$[33] were prepared by following literature methods.

$Al(^iBu)_2[N(Ph)NN(Ph)]$ (1). To a slurry of (Ph)NNN(H)(Ph) (3.40 g, 17.3 mmol) in pentane (150 mL) at −78 °C was added, dropwise, a pentane (50 mL) solution of $AlH(^iBu)_2$ (17.5 mL, 1 M solution in hexane,

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(32) Hartman, W. W.; Dickey, J. B. *Org. Synth.* **1943**, *2*, 163.

(33) (a) Forbes, E. J.; Richardson, R. D.; Tatlow, T. C. *Chem. Ind.* **1959**, 630. (b) Brooke, G. M.; Burden, J.; Stacey, M.; Tatlow, T. C. *J. Chem. Soc.* **1960**, 1768.

Table IX. Summary of X-ray Diffraction Data[a]

compd	$Al(Bu^i)_2[N(Ph)NN(Ph)]$	$Al(BHT)_2[N(Ph)NN(Ph)]$	AlMe(salen)·MeCN	$Al[N(2\text{-}MePh)NN(2\text{-}MePh)]\cdot C_7H_8$	$Al[N(4\text{-}MeOPh)NN(4\text{-}MeOPh)]_3$	$Al[N(4\text{-}ClPh)NN(4\text{-}ClPh)]_3$	$HN(C_6F_5)NN(C_6F_5)$	$(2\text{-}MePh)NNN(H)\text{-}(2\text{-}MePh)\text{-}(2\text{-}MePhNH_2)$
formula	$C_{20}H_{28}AlN_3$	$C_{42}H_{56}AlN_3O_2$	$C_{19}H_{20}AlN_3O_2$	$C_{40}H_{50}AlN_9$	$C_{42}H_{42}AlN_9O_6$	$C_{36}H_{24}AlCl_6N_9$	$C_{12}HF_{10}N_3$	$C_{21}H_{24}N_4$
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/c$	$I4_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	12.437(7)	17.967(6)	11.751(8)	11.392(3)	27.996(6)	8.746(3)	10.027(4)	9.609(9)
b, Å	12.327(5)	10.030(5)	12.227(9)	11.418(3)		18.754(4)	9.909(4)	10.272(5)
c, Å	13.413(9)	21.650(6)	12.609(9)	31.227(9)	20.613(5)	22.985(5)	12.998(4)	11.276(9)
α, deg								108.53(8)
β, deg	98.29(5)	99.99(2)	98.52(6)	94.31(2)		90.36(3)	96.00(3)	114.90(7)
γ, deg								90.88(7)
V, Å^3	2035(2)	3842(3)	1792(2)	4051(2)	16 156(8)	3770(2)	1284.4(8)	942(1)
Z	4	2	4	4	16	4	4	2
D(calcd), g cm^{-3}	1.101	1.430	1.295	1.223	1.309	1.449	1.950	1.171
crystal dimens, mm	0.30 × 0.32 × 0.35	0.40 × 0.41 × 0.41	0.40 × 0.24 × 0.34	0.41 × 0.40 × 0.26	0.43 × 0.38 × 0.40	0.14 × 0.14 × 0.23	0.42 × 0.42 × 0.40	0.40 × 0.31 × 0.35
temp, K	193	193	193	193	193	193	298	298
μ, cm^{-1}	1.01	0.07	0.130	1.584	0.110	0.520	0.222	0.071
2θ limits, deg	4.0–45.0	4.0–45.0	4.0–40.0	4.0–40.0	4.0–40.0	4.0–40.0	4.0–40.0	4.0–40.0
no. of data collected	3116	2022	1930	4541	5839	4219	1435	1898
no. of unique data	2641	1801	1651	3790	5293	3545	1401	1875
no. of obsd data	2169 [$F > 4\sigma(F)$]	1621 [$F > 5\sigma(F)$]	1334 [$F > 4\sigma(F)$]	2166 [$F > 4\sigma(F)$]	2171 [$F > 4\sigma(F)$]	2808 [$F > 4\sigma(F)$]	1206 [$F > 4\sigma(F)$]	1496 [$F > 4\sigma(F)$]
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0083F^2$	$w^{-1} = \sigma^2(F) + 0.0512F^2$	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F) + 0.0006F^2$	$w^{-1} = \sigma^2(F) + 0.0011F^2$	$w^{-1} = \sigma^2(F) + 0.0010F^2$	$w^{-1} = \sigma^2(F) + 0.0015F^2$	$w^{-1} = \sigma^2(F)$
R	0.059	0.086	0.082	0.093	0.076	0.042	0.034	0.070
R_w	0.071	0.090	0.082	0.099	0.077	0.056	0.046	0.070
final residual, e Å^{-3}	0.30	0.40	0.49	0.62	0.33	0.41	0.15	0.20

[a] Radiation: Mo Kα (λ = 0.710 73 Å), graphite monochromator.

Table X. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3 Å^2) for $Al(^iBu)_2[N(Ph)NN(Ph)]$ (1)

	x	y	z	U(eq)[a]
Al(1)	7058(1)	2571(1)	843(1)	35(1)
N(1)	7686(2)	3727(2)	1762(2)	38(1)
N(12)	8611(2)	3767(2)	1391(2)	35(1)
N(2)	8549(2)	2995(2)	703(2)	36(1)
C(11)	7543(2)	4449(2)	2541(2)	33(1)
C(12)	6614(3)	4313(3)	2999(2)	41(1)
C(13)	6428(3)	4975(3)	3783(3)	48(1)
C(14)	7169(3)	5774(3)	4135(3)	52(1)
C(15)	8093(3)	5925(3)	3680(3)	48(1)
C(16)	8279(3)	5268(2)	2874(3)	41(1)
C(21)	9403(2)	2878(3)	137(2)	34(1)
C(22)	10292(3)	3586(3)	213(2)	40(1)
C(23)	11084(3)	3429(3)	−397(3)	46(1)
C(24)	11012(3)	2578(3)	−1074(3)	50(1)
C(25)	10135(3)	1868(3)	−1136(3)	50(1)
C(26)	9346(3)	2017(3)	−537(3)	44(1)
C(31)	6761(3)	1205(3)	1493(3)	41(1)
C(32)	7625(6)	384(7)	1927(7)	48(3)
C(33)	8611(5)	792(5)	2396(6)	128(3)
C(34)	7210(13)	−638(9)	2403(10)	68(5)
C(35)	7541(6)	861(6)	2404(6)	43(3)
C(36)	7109(10)	−224(9)	2784(10)	70(5)
C(41)	6087(3)	3114(3)	−323(2)	40(1)
C(42)	4880(3)	2853(3)	−394(3)	41(1)
C(43)	4429(3)	3316(3)	511(3)	58(1)
C(44)	4247(4)	3265(4)	−1375(3)	75(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

17.5 mmol). The resulting solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under vacuum to give a viscous red-brown liquid, which crystallized upon standing at room temperature. Orange crystals suitable for X-ray diffraction were obtained by dissolving the product in pentane (10 mL) followed by crystallization and removal of the solvent at low temperature (−78 °C). Yield: 4.6 g, 79%. Mp: 35–37 °C. Anal. Calc for $C_{20}H_{28}AlN_3$: C, 71.9; H, 8.36; N, 12.45. Found: C, 70.61; H, 8.11; N, 12.03. MS [EI, *m/z* (assignment, %)]: 337 (M$^+$, 35), 280 (M$^+$ − ^{i}Bu, 50). IR (Nujol, cm^{-1}): 1597 (s), 1495 (s), 1486 (s), 1362 (m), 1340 (s), 1324 (s), 1308 (s), 1298 (s), 1210 (s), 1071 (m), 897 (m), 849 (m), 815 (m), 758 (s), 689 (s), 676 (s), 512 (m). NMR (C_6D_6, δ): ^{1}H, 7.36 [4H, d, *J*(H–H) = 8.1 Hz, o-C*H*], 7.12 [4H, m, *J*(H–H) = 8.3 Hz, m-C*H*], 6.92 [2H, t, *J*(H–H) = 7.9 Hz, p-C*H*], 2.01 [2H, m, *J*(H–H) = 7.0 Hz, AlCH$_2$C*H*], 1.01 [12H, d, *J*(H–H) = 7.0 Hz, AlCH$_2$CH(C*H*$_3$)$_2$], 0.49 [4H, d, *J*(H–H) = 7.0 Hz, AlC*H*$_2$]; ^{13}C, 144.5 (N*C*), 129.8 (m-*C*H), 125.8 (p-*C*H), 117.8 (o-*C*H), 28.2 [AlCH$_2$CH(*C*H$_3$)$_2$], 26.3 (AlCH$_2$*C*H), 21.9 (Al*C*H$_2$).

$Al(^iBu)[N(Ph)NN(Ph)]_2$ (2). To a solution of $AlH(^iBu)_2$ (10.0 mL, 1 M solution in hexane, 10.0 mmol) in hexane (75 mL) was added, dropwise, (Ph)NNN(H)(Ph) (3.80 g, 19.3 mmol) in toluene (100 mL). The reaction mixture was warmed to room temperature and then stirred overnight. The volume was reduced by half and any precipitate filtered off. The solvent was removed under vacuum to give an orange-red solid. Yield: 3.22 g, 70%. Mp: 124–126 °C. Anal. Calcd for $C_{28}H_{29}AlN_6$: C, 70.57; H, 6.13; N, 17.63. Found: C, 70.54; H, 6.22; N, 17.68. MS [EI, *m/z* (assignment, %)]: 419 (M$^+$ − ^{i}Bu, 5). IR (Nujol, cm^{-1}): 1595 (m), 1484 (m), 1362 (m), 1302 (s), 1286 (s), 1238 (m), 1210 (m), 1074 (w), 758 (s), 687 (s), 669 (m), 656 (m), 548 (w), 512 (w), 450 (w). NMR (C_6D_6, δ): ^{1}H, 7.50 [8H, d, *J*(H–H) = 8.0 Hz, o-C*H*], 7.06 [8H, t, *J*(H–H) = 8.0 Hz, m-C*H*], 6.91 [4H, t, *J*(H–H) = 7.9 Hz, p-C*H*], 2.02 [1H, m, *J*(H–H) = 7.0 Hz, AlCH$_2$C*H*], 1.00 [6H, d, *J*(H–H) = 7.0 Hz, AlCH$_2$CH(C*H*$_3$)$_2$], 0.63 [2H, d, *J*(H–H) = 7.0 Hz, AlC*H*$_2$]; ^{13}C, 145.0 (N*C*), 129.5 (m-*C*H), 125.7 (p-*C*H), 119.2 (o-*C*H), 28.3 [AlCH$_2$CH(*C*H$_3$)$_2$], 26.3 (AlCH$_2$*C*H), 22.0 (Al*C*H$_2$); ^{27}Al, 47 ($W_{1/2}$ = 4500 Hz).

$Al(^tBu)_2[N(Ph)NN(Ph)]$ (3). A solution of $Al(^tBu)_3$ (0.54 g, 2.75 mmol) in hexane (20 mL) was cooled to −78 °C, and (Ph)NNN(H)(Ph) (0.542 g, 2.75 mmol) in toluene (20 mL) was added dropwise *via* cannula. After the addition was complete, the reaction was warmed to room temperature and stirred for 1 h. Removal of the volatiles under vacuum gave a dark orange-brown solid. Yield: 0.66 g, 71%. Mp: 88–90 °C. Anal. Calc for $C_{20}H_{25}AlN_3$: C, 71.19; H, 8.36; N, 12.45. Found: C,

Table XI. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3 Å^2) for Al(BHT)$_2$[N(Ph)NN(Ph)] (**6**)

	x	*y*	*z*	*U*(eq)[a]
Al(1)	0	1709(2)	7500	18(1)
O(1)	−779(1)	926(3)	7121(1)	24(1)
N(1)	309(2)	3353(3)	7127(1)	21(1)
N(2)	0	4112(5)	7500	28(2)
C(1)	582(2)	4012(4)	6627(2)	23(2)
C(2)	1254(3)	3629(4)	6477(2)	31(2)
C(3)	1510(3)	4252(5)	5978(2)	48(2)
C(4)	1097(3)	5241(5)	5646(2)	47(2)
C(5)	420(3)	5643(5)	5810(2)	41(2)
C(6)	162(3)	5036(4)	6302(2)	33(2)
C(7)	−1126(2)	−129(4)	6784(2)	21(1)
C(8)	−1381(2)	−1219(4)	7100(2)	20(1)
C(9)	−1625(2)	−2340(4)	6747(2)	27(2)
C(10)	−1652(2)	−2403(4)	6100(2)	29(2)
C(11)	−1468(2)	−1266(4)	5802(2)	26(2)
C(12)	−1221(2)	−87(4)	6122(2)	22(1)
C(13)	−1408(2)	−1228(4)	7811(2)	24(1)
C(14)	−606(3)	−1322(5)	8179(2)	48(2)
C(15)	−1842(3)	−2426(5)	7997(2)	42(2)
C(16)	−1807(3)	5(5)	7979(2)	54(2)
C(17)	−1902(3)	−3649(5)	5741(2)	48(2)
C(18)	−1094(2)	1156(4)	5744(2)	28(2)
C(19)	−242(3)	1383(5)	5760(2)	37(2)
C(20)	−1442(3)	1000(5)	5050(2)	50(2)
C(21)	−1457(3)	2390(5)	5982(2)	38(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table XII. Fractional Atomic Coordinate (×10^4) and Isotropic Thermal Parameters (×10^3 Å^2) for AlMe(salen)·MeCN

	x	*y*	*z*	*U*(eq)[a]
Al(1)	7663(3)	3666(2)	9928(2)	29(1)
C(1)	7053(9)	2346(8)	10511(8)	38(4)
O(11)	6652(5)	4697(5)	9393(5)	34(2)
O(21)	8080(6)	4526(5)	11103(5)	36(3)
N(11)	7656(6)	3120(6)	8398(6)	23(3)
N(21)	9366(6)	3437(6)	9870(6)	20(3)
C(11)	5931(8)	4793(7)	8485(7)	26(4)
C(12)	4994(8)	5534(7)	8423(7)	31(4)
C(13)	4252(9)	5654(8)	7471(8)	34(4)
C(14)	4410(10)	5063(8)	6546(8)	45(4)
C(15)	5279(9)	4341(8)	6602(7)	32(4)
C(16)	6067(8)	4190(7)	7544(7)	29(4)
C(17)	6991(8)	3408(7)	7538(7)	30(4)
C(18)	8588(8)	2347(7)	8317(7)	29(4)
C(21)	9008(10)	4602(7)	11812(7)	29(4)
C(22)	8981(9)	5132(7)	12791(7)	32(4)
C(23)	9929(11)	5277(8)	13529(8)	44(5)
C(24)	11004(11)	4899(8)	13308(8)	45(5)
C(25)	11085(10)	4385(7)	12345(7)	39(4)
C(26)	10090(9)	4218(7)	11591(7)	27(4)
C(27)	10205(9)	3690(7)	10599(7)	30(4)
C(28)	9660(9)	2905(7)	8895(7)	34(4)
N(1)	2455(8)	6939(8)	5039(7)	50(4)
C(2)	1956(11)	7394(9)	5578(8)	43(4)
C(3)	1307(10)	7994(10)	6258(9)	67(5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table XIII. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3 Å^2) for Al[N(2-MePh)NN(2-MePh)]$_3$·C$_7$H$_8$ (**9**)

	x	*y*	*z*	*U*(eq)[a]
Al(1)	1935(3)	1090(3)	3594(1)	36(1)
N(1)	525(8)	2081(8)	3641(3)	37(4)
N(12)	1063(10)	3082(8)	3549(3)	43(4)
N(2)	2130(8)	2767(7)	3453(3)	37(4)
N(3)	2699(8)	1201(8)	4182(2)	39(4)
N(34)	3676(8)	680(8)	4093(3)	43(4)
N(4)	3577(7)	515(7)	3671(3)	34(3)
N(5)	1323(7)	−549(7)	3616(3)	34(4)
N(56)	1290(7)	−694(8)	3198(3)	40(4)
N(6)	1546(7)	333(8)	3034(2)	34(3)
C(11)	−641(10)	2231(10)	3781(3)	42(3)
C(12)	−816(11)	3129(11)	4092(4)	63(4)
C(13)	−1902(13)	3193(13)	4250(5)	93(5)
C(14)	−2747(13)	2459(12)	4105(4)	77(4)
C(15)	−2680(12)	1620(11)	3807(4)	70(4)
C(16)	−1515(12)	1491(12)	3636(4)	67(4)
C(17)	−1387(11)	644(12)	3318(5)	96(7)
C(21)	2973(11)	3683(11)	3364(4)	50(3)
C(22)	4128(10)	3459(11)	3556(3)	57(4)
C(23)	5008(14)	4243(12)	3477(4)	91(5)
C(24)	4658(13)	5241(12)	3239(4)	75(4)
C(25)	3579(11)	5466(11)	3070(4)	62(4)
C(26)	2665(13)	4623(12)	3125(4)	69(4)
C(27)	1538(11)	4847(12)	2915(4)	74(6)
C(31)	2648(9)	1593(10)	4614(3)	45(3)
C(32)	2246(10)	2704(10)	4660(4)	53(3)
C(33)	2093(11)	3200(12)	5069(4)	78(4)
C(34)	2398(11)	2478(12)	5408(4)	69(4)
C(35)	2775(10)	1390(11)	5378(4)	59(4)
C(36)	2921(10)	883(11)	4966(3)	46(3)
C(37)	3288(11)	−355(11)	4939(4)	72(6)
C(41)	4430(9)	−241(10)	3506(3)	33(3)
C(42)	4848(9)	−1205(9)	3747(3)	42(3)
C(43)	5619(10)	−1964(11)	3579(4)	56(4)
C(44)	5990(10)	−1760(10)	3172(3)	56(4)
C(45)	5588(9)	−830(10)	2936(3)	47(3)
C(46)	4802(10)	−24(10)	3101(3)	42(3)
C(47)	4437(9)	1036(9)	2840(3)	50(5)
C(51)	1263(9)	−1569(9)	3864(3)	35(3)
C(52)	1725(10)	−2620(10)	3732(4)	50(3)
C(53)	1659(10)	−3626(11)	3984(4)	64(4)
C(54)	1153(11)	−3558(11)	4370(4)	67(4)
C(55)	689(10)	−2528(10)	4505(4)	54(4)
C(56)	728(9)	−1503(10)	4259(3)	36(3)
C(57)	176(10)	−390(10)	4402(3)	52(5)
C(61)	1465(9)	460(9)	2581(3)	37(3)
C(62)	1101(9)	1553(10)	2438(3)	50(3)
C(63)	1018(10)	1833(11)	2005(4)	59(4)
C(64)	1346(10)	1001(11)	1726(4)	59(4)
C(65)	1708(9)	−74(10)	1851(3)	46(3)
C(66)	1806(10)	−384(11)	2300(3)	51(3)
C(67)	2270(10)	−1548(10)	2439(3)	61(5)
C(1)	4449(39)	8505(34)	−269(12)	220(22)
C(2)	4626	9503	−95	49
C(3)	4937	9618	344	123
C(4)	5369	10683	508	247
C(5)	5490	11633	234	115
C(6)	5179	11518	−204	252
C(7)	4748	10453	−369	175

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

71.10; H, 8.21; N, 12.48. IR (KBr, cm^{-1}): 2922 (m), 2833 (m), 2864 (s), 1596 (s), 1489 (s), 1486 (s), 1465 (s), 1447 (m), 1414 (m), 1324 (m), 1310 (s), 1300 (s), 1283 (s), 1246 (m), 1209 (m), 1172 (w), 814 (m), 758 (s), 689 (s), 676 (w), 676 (w), 611 (m), 500 (w). NMR (C$_6$D$_6$, δ): ^{1}H, 7.38 [4H, d, *J*(H–H) = 8.7 Hz, o-C*H*], 7.10 [4H, m, *J*(H–H) = 7.5 Hz, m-C*H*], 6.91 [2H, t, *J*(H–H) = 7.3 Hz, p-C*H*], 1.14 [18H, s, AlC(C*H*$_3$)$_3$]; ^{13}C, 144.6 (N*C*), 129.8 (m-*C*H), 125.9 (p-*C*H), 117.8 (o-*C*H), 29.4 [AlC(*C*H$_3$)$_3$], 14.9 [Al*C*(CH$_3$)$_3$]; ^{27}Al, 91 ($W_{1/2}$ = 8460 Hz).

AlMe(BHT)[N(Ph)NN(Ph)] (4). A solution of (Ph)NNN(H)(Ph) (1.02 g, 5.17 mmol) in toluene (10 mL) was added dropwise to a toluene solution (15 mL) of AlMe$_2$(BHT)(OEt$_2$) (1.809 g, 5.16 mmol) maintained at −78 °C. A dark brown solution formed, which was left to stir at −78 °C for 30 min and then warmed to room temperature. After 2 h at room temperature, the solvent was removed in vacuo, leaving a sticky brown solid. Washing with pentane and drying under vacuum at 40 °C gave a brown powder. Yield: 1.98 g, 84%. Mp: 114–116 °C. Anal. Calc for C$_{28}$H$_{36}$AlN$_3$O: C, 73.49; H, 7.93; N, 9.18. Found: C, 69.10; H, 7.91; N, 8.77. IR (KBr, cm^{-1}): 2957 (m), 1602 (m), 1488 (m), 1465 (m), 1427 (m), 1309 (s), 1301 (s), 1284 (m), 761 (s), 691 (s), 669 (m), 502 (w). NMR (CDCl$_3$, δ): ^{1}H, 7.26, 7.21 (8H, m, o- and m-C*H*), 7.04 [2H, t, *J*(H–H) = 7.0 Hz, p-C*H*], 6.81 (2H, s, C$_6$*H*$_2$), 2.06 (3H, s, C*H*$_3$), 1.17 [18H, s, C(C*H*$_3$)$_3$], −0.39 (3H, s, Al(C*H*$_3$); ^{13}C, 152.3 (O*C*), 143.4 (N*C*), 138.2, 126.9, 126.0 (*C*$_6$H$_2$), 129.2, 125.7, 118.9 (*C*$_6$H$_5$), 34.7 (p-*C*H$_3$), 30.8 [C(*C*H$_3$)$_3$], 21.1 [*C*(CH$_3$)$_3$], −9.9 (Al*C*H$_3$).

Table XIV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3 Å^2) for Al[N(4-MeOPh)NN(4-MeOPh)]$_3$ (**11**)

	x	*y*	*z*	*U*(eq)[a]
Al(1)	8328(1)	6384(1)	932(2)	32(1)
N(1)	8680(3)	6969(3)	1198(4)	27(3)
N(12)	9105(3)	6764(3)	1192(4)	35(3)
N(2)	9032(3)	6314(3)	1023(4)	28(3)
N(3)	8156(3)	6174(3)	1805(4)	33(3)
N(34)	8075(3)	5702(3)	1623(4)	35(3)
N(4)	8140(3)	5697(3)	978(4)	30(3)
N(5)	7707(3)	6635(3)	588(4)	33(3)
N(56)	7855(3)	6666(3)	–8(4)	35(3)
N(6)	8306(3)	6525(3)	–6(3)	31(3)
C(11)	8676(3)	7455(3)	1392(4)	27(3)
C(12)	8236(3)	7688(3)	1419(4)	33(3)
C(13)	8213(4)	8162(3)	1607(5)	39(3)
C(14)	8617(4)	8415(4)	1775(5)	41(3)
C(15)	9047(4)	8173(3)	1768(5)	41(3)
C(16)	9086(3)	7698(3)	1578(5)	34(3)
O(1)	8639(3)	8880(3)	1952(4)	50(3)
C(17)	8203(3)	9122(4)	2034(5)	50(5)
C(21)	9437(3)	6020(3)	957(5)	28(3)
C(22)	9905(4)	6170(4)	1033(5)	45(3)
C(23)	10276(4)	5850(4)	982(5)	47(3)
C(24)	10197(4)	5379(4)	838(5)	41(3)
C(25)	9731(3)	5231(4)	729(5)	39(3)
C(26)	9356(3)	5544(3)	783(5)	36(3)
O(2)	10536(3)	5032(3)	803(4)	55(3)
C(27)	11013(4)	5180(5)	786(6)	79(6)
C(31)	8112(3)	6246(3)	2476(5)	29(3)
C(32)	8135(3)	6719(3)	2670(5)	35(3)
C(33)	8129(3)	6848(4)	3325(5)	35(3)
C(34)	8078(3)	6489(4)	3782(5)	35(3)
C(35)	8045(3)	6012(3)	3588(5)	34(3)
C(36)	8065(3)	5894(3)	2947(5)	29(3)
O(3)	8067(3)	6563(2)	4441(3)	50(3)
C(37)	8173(4)	7033(4)	4659(5)	62(5)
C(41)	8087(3)	5251(4)	683(5)	33(3)
C(42)	8258(3)	4832(3)	964(5)	34(3)
C(43)	8198(3)	4395(3)	651(5)	37(3)
C(44)	7987(4)	4381(4)	47(5)	40(3)
C(45)	7826(3)	4799(4)	–238(5)	37(3)
C(46)	7884(3)	5231(4)	71(5)	43(3)
O(4)	7911(3)	3970(3)	–297(3)	56(3)
C(47)	8043(5)	3528(4)	4(5)	70(6)
C(51)	7209(3)	6699(3)	698(5)	28(3)
C(52)	7048(3)	6727(3)	1327(5)	29(3)
C(53)	6560(3)	6779(3)	1435(5)	37(3)
C(54)	6247(3)	6816(3)	926(5)	31(3)
C(55)	6406(4)	6801(3)	294(5)	36(3)
C(56)	6891(3)	6743(3)	178(5)	32(3)
O(5)	5768(3)	6872(3)	1097(3)	45(3)
C(57)	5435(4)	6911(4)	576(5)	55(5)
C(61)	8563(4)	6599(3)	–579(5)	36(3)
C(62)	8393(4)	6899(3)	–1083(5)	37(3)
C(63)	8663(4)	6971(3)	–1644(5)	45(3)
C(64)	9108(4)	6771(4)	–1706(6)	48(3)
C(66)	9276(4)	6472(4)	–1226(5)	48(3)
C(66)	9006(3)	6388(3)	–664(5)	42(3)
O(6)	9347(3)	6875(3)	–2271(3)	66(3)
C(67)	9832(4)	6733(5)	–2316(6)	82(6)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table XV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3 Å^2) for Al[N(4-ClPh)NN(4-ClPh)]$_3$ (**13**)

	x	*y*	*z*	*U*(eq)[a]
Al(1)	7025(2)	2859(1)	4020(1)	25(1)
N(1)	7997(4)	1913(2)	4035(2)	23(1)
N(12)	6879(4)	1588(2)	3752(2)	26(1)
N(2)	5893(4)	2086(2)	3615(2)	25(1)
N(3)	5712(4)	2848(2)	4725(2)	24(1)
N(34)	4951(4)	3425(2)	4581(2)	28(1)
N(4)	5476(4)	3617(2)	4070(2)	26(1)
N(5)	8725(4)	3454(2)	4330(2)	25(1)
N(56)	9247(4)	3643(2)	3814(2)	28(1)
N(6)	8338(4)	3327(2)	3435(2)	25(1)
C(11)	9256(5)	1502(2)	4214(2)	24(1)
C(12)	10511(5)	1851(3)	4450(2)	30(1)
C(13)	11762(6)	1473(3)	4644(2)	34(1)
C(14)	11764(6)	743(3)	4606(2)	41(1)
C(15)	10525(6)	386(3)	4380(2)	50(2)
C(16)	9256(6)	762(3)	4176(2)	42(1)
Cl(1)	13330(2)	258(1)	4848(1)	75(1)
C(21)	4486(5)	1856(3)	3370(2)	25(1)
C(22)	4052(5)	1143(3)	3352(2)	33(1)
C(23)	2634(6)	957(3)	3125(2)	39(1)
C(24)	1668(6)	1477(3)	2925(2)	36(1)
C(25)	2081(6)	2184(3)	2932(2)	39(1)
C(25)	2081(6)	2184(3)	2932(2)	39(1)
C(26)	3503(6)	2374(3)	3158(2)	36(1)
C1(2)	–144(1)	1243(1)	2668(1)	50(1)
C(31)	5283(5)	2499(2)	5244(2)	24(1)
C(32)	5973(5)	1858(3)	5365(2)	35(1)
C(33)	5588(6)	1478(3)	5862(2)	38(1)
C(34)	4511(6)	1751(3)	6231(2)	38(1)
C(35)	3817(6)	2394(3)	6123(2)	40(1)
C(36)	4194(6)	2772(3)	5624(2)	37(1)
C1(3)	4044(2)	1278(1)	6856(1)	63(1)
C(41)	4957(5)	4267(2)	3836(2)	23(1)
C(42)	4374(5)	4810(3)	4179(2)	31(1)
C(43)	3944(6)	5445(3)	3931(2)	39(1)
C(44)	4089(5)	5538(3)	3334(2)	33(1)
C(45)	4659(5)	5007(3)	2991(2)	33(1)
C(46)	5108(5)	4371(3)	3242(2)	29(1)
Cl(4)	3615(2)	6359(1)	3027(1)	52(1)
C(51)	9534(5)	3697(2)	4820(2)	26(1)
C(52)	9110(6)	3439(3)	5357(2)	33(1)
C(53)	9855(6)	3658(3)	5867(2)	38(1)
C(54)	11033(6)	4135(3)	5827(2)	35(1)
C(55)	11495(6)	4390(3)	5293(2)	39(1)
C(56)	10764(5)	4176(3)	4788(2)	35(1)
Cl(5)	11975(2)	4420(1)	6449(1)	55(1)
C(61)	8669(5)	3426(3)	2842(2)	29(1)
C(62)	9679(5)	3954(3)	2645(2)	36(1)
C(63)	10023(6)	3981(3)	2059(2)	38(1)
C(64)	9404(5)	3489(3)	1677(2)	34(1)
C(65)	8356(6)	2997(3)	1865(2)	37(1)
C(66)	7991(5)	2967(3)	2450(2)	31(1)
Cl(6)	9954(2)	3489(1)	952(1)	49(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Al(BHT)[N(Ph)NN(Ph)]$_2$ (5). $AlH_2(BHT)(NMe_3)$ (1.00 g, 3.27 mmol) was dissolved in toluene (10 mL), the solution was cooled in an ice bath, and (Ph)NNN(H)(Ph) (1.29 g, 6.54 mmol) in toluene (20 mL) was added dropwise over a period of 30 min. After 12 h of stirring, the solvent was removed, and the brown residue was washed once with pentane (20 mL) and then vacuum-dried. Yield: 1.20 g, 57%. Mp: 188–190 °C. Anal. Calc for $C_{39}H_{43}AlN_6O$: C, 73.33; H, 6.78; N, 13.16. Found: C, 71.27; H, 6.89; N, 12.85. IR (KBr, cm^{-1}): 2914 (w), 2870 (w), 1604 (m), 1501 (m), 1486 (m), 1467 (m), 1443 (m), 1427 (m), 1413 (m), 1328 (m), 1311 (s), 1283 (s), 1247 (s), 1203 (m), 764 (m), 753 (m), 687 (m). NMR ($CDCl_3$, δ): ^{1}H, 7.27 [8H, d, *J*(H–H) = 8.1 Hz, o-C*H*], 7.18 [8H, m, *J*(H–H) = 7.9 Hz, m-C*H*], 7.08 [4H, t, *J*(H–H) = 7.6 Hz, p-C*H*], 7.01 (2H, s, C_6H_2), 2.25 (3H, s, CH_3), 1.33 [18H, s, $C(CH_3)_3$]; ^{13}C, 152.5 (O*C*), 143.9 (N*C*), 138.5, 127.5, 126.0 (C_6H_2), 129.2, 126.5, 120.0 (C_6H_5), 34.8 (p-CH_3), 31.6 [$C(CH_3)_3$], 21.1 [$C(CH_3)_3$]; ^{27}Al, 35 ($W_{1/2}$ = 4300 Hz).

Al(BHT)$_2$[N(Ph)NN(Ph)] (6). $AlMe(BHT)_2$ (2.00 g, 4.16 mmol) was dissolved in toluene (20 mL), and a solution of (Ph)NNN(H)(Ph) (0.82 g, 4.16 mmol) in toluene (10 mL) was added dropwise. A deep red solution formed, which was stirred for 3 h. Removal of the solvent under vacuum gave a thick, red oil, which was triturated with pentane (15 mL) to give an orange solid. The red pentane solution was decanted and the solid washed once more with cold (–30 °C) pentane (15 mL). Drying in vacuum gave a yellow powder. X-ray-quality crystals were obtained by recrystallization from hexane. Yield: 1.04 g, 38%. Mp: 160–161 °C. Anal. Calc for $C_{42}H_{56}AlN_3O_2$: C, 76.21; H, 8.53; N, 6.35. Found: C, 75.70; H, 8.75; N, 6.21. IR (KBr, cm^{-1}): 2957 (m), 2917 (m), 2868 (m), 1602 (m), 1485 (w), 1424 (m), 1390 (w), 1360 (w), 1303 (s), 1287 (s), 1266 (s), 1251 (s), 1209 (m), 926 (w), 891 (w), 859 (w), 767 (m), 755 (m), 693 (m). NMR ($CDCl_3$, δ): ^{1}H, 7.48 [4H, d, *J*(H–H) = 7.7 Hz, o-C*H*], 7.33 [4H, m, *J*(H–H) = 7.3 Hz, m-C*H*], 7.21 [2H, t, *J*(H–

H) = 7.0 Hz, p-C*H*], 6.94 (4H, s, C_6H_2), 2.21 (6H, s, CH_3), 1.30 [36H, s, $C(CH_3)_3$]; ^{13}C, 151.7 (*O*C), 143.1 (*N*C), 138.3, 127.3, 126.5 (C_6H_2), 129.0, 126.1, 120.5 (C_6H_5), 35.0 (p-CH_3), 31.5 [$C(CH_3)_3$], 21.1 [$C(CH_3)_3$]; ^{27}Al, 31 ($W_{1/2}$ = 7300 Hz).

Al(^{i}Bu)(salen) (7). A solution of Al(^{i}Bu)$_2$[N(Ph)NN(Ph)] (0.50 g, 1.50 mmol) in pentane (50 mL) was added to a solution of H_2salen (0.475 g, 1.77 mmol) in pentane/THF (15 mL, 25 mL). As the addition proceeded, the solution color changed from amber to golden yellow. The flask was placed in a freezer at −24 °C overnight, after which the yellow needlelike crystals that had formed were isolated by filtration. Yield: 0.185 g, 36%. MS [EI, *m/z* (assignment, %)]: 293 (M$^+$ − ^{i}Bu, 100). NMR (C_6D_6, *δ*): ^{1}H, 8.24 (2H, s, N=C*H*), 7.36 (2H, m, C_6H_4), 7.10 (4H, m, C_6H_4), 6.69 (2H, m, C_6H_4), 3.69 (2H, m, C_2H_4), 3.99 (2H, m, C_2H_4), 1.53 [1H, m, *J*(H–H) = 6.5 Hz, $AlCH_2CH$], 0.69 [6H, d, *J*(H–H) = 6.5 Hz, $AlCH_2CH(CH_3)_2$], −0.29 [2H, d, *J*(H–H) = 6.8 Hz, $AlCH_2$].

Al(salen)[N(Ph)NN(Ph)] (8). A solution of AlMe(salen) in MeCN (30 mL) was prepared from H_2salen (0.910 g, 3.40 mmol) and $AlMe_3$ (3.4 mL, 1.0 M hexane solution, 3.4 mmol) as described previously. A solution of 1,3-diphenyltriazene (0.672 g, 3.40 mmol) in MeCN (20 mL) was added to the above dropwise, *via* cannula. The clear orange reaction mixture was then refluxed until the reaction was complete, as judged by the precipitation of an orange solid. Additional MeCN was added, with heating, to dissolve the bulk of the precipitated material. After filtration, the hot solution was cooled slowly to room temperature and then to −24 °C overnight. Orange needles of **8**·$^1/_2$MeCN were isolated by filtration and vacuum-drying. Yield: 1.08 g, 62%. Mp: 226–227 °C. IR (KBr, cm^{-1}): 3044 (w), 2938 (w), 2251 (w), 1645 (m), 1632 (s), 1603 (m), 1547 (s), 1475 (m), 1455 (m), 1409 (w), 1394 (w), 1330 (m), 1303 (s), 1279 (s), 1246 (m), 1208 (m), 907 (m), 759 (s), 693 (m), 641 (m), 632 (m). NMR ($CDCl_3$, *δ*): ^{1}H, 8.25 (2H, s, N=C*H*), 7.31 (2H, m, C_6H_4), 7.22 [4H, d, *J*(H–H) = 8.1 Hz, o-C*H*], 7.12 (6H, m, m-C*H* and C_6H_4), 6.98 [2H, t, *J*(H–H) = 8.5 Hz, p-C*H*], 6.62 (2H, m, C_6H_4), 4.02 (2H, m, C_2H_4), 3.55 (2H, m, C_2H_4); ^{27}Al, 11 ($W_{1/2}$ = 940 Hz).

Synthesis of 1,3-Diaryltriazene Ligands. All ligands were prepared by procedures adapted from the literature, through one of two methods: method 1, diazotization and coupling of anilines with aqueous $NaNO_2$/HCl, followed by neutralization with NaO_2CMe;[32] method 2, diazotization and coupling of anilines employing isoamyl nitrite in Et_2O. The crude triazenes were purified by crystallization in the presence of activated charcoal in order to remove traces of isomeric aminoazobenzene side products.[34] Yields given are those after crystallization from the stated solvent(s), and characterization by IR and ^{1}H NMR spectroscopy follows.

(2-MePh)NNN(H)(2-MePh). Prepared by method 2, the compound crystallizes from hexane with one molecule of 2-methylaniline. Yield: 30%, based on amount of triazene formed. Mp: 56 °C. IR (KBr, cm^{-1}): 3430 (w), 3389 (w), 3185 (w), 2972 (w), 1589 (m), 1527 (m), 1513 (m), 1501 (m), 1483 (m), 1159 (m), 1407 (m), 1248 (s), 1213 (s), 1186 (m), 1174 (m), 755 (s), 715 (m). NMR ($CDCl_3$, *δ*): ^{1}H, 9.53 (1H, br s, N*H*), 7.61 (2H, m, C_6H_4), 7.23 (5H, m, C_6H_4), 7.07 (1H, m, C_6H_4), 7.04, 6.70 [2H, 2H, m, C_6H_4, (2-MePh)NH_2], 3.54 (2H, br s, NH_2), 2.41 (6H, br s, CH_3), 2.17 [3H, s, CH_3, (2-MePh)NH_2].

(4-MePh)NNN(H)(4-MePh).[35] Prepared by method 1. Yield: 82% (hexane). Mp: 115 °C. IR (KBr, cm^{-1}): 3200 (w), 2920 (w), 1600 (m), 1525 (s), 1501 (m), 1436 (m), 1397 (m), 1309 (m), 1294 (m), 1245 (s), 1193 (m), 1176 (m), 813 (s), 655 (w), 613 (w), 506 (w). NMR ($CDCl_3$, *δ*): ^{1}H, 9.54 (1H, br s, N*H*), 7.29 [4H, d, *J*(H–H) = 8.3 Hz, o-C*H*], 7.16 [4H, d, *J*(H–H) = 8.3 Hz, m-C*H*], 2.35 (6H, s, CH_3).

(4-MeOPh)NNN(H)(4-MeOPh).[35] Prepared by method 1. Yield: 80% (hexane). Mp: 97 °C. IR (KBr, cm^{-1}): 3167 (w), 2961 (w), 2835 (w), 1603 (m), 1539 (m), 1509 (s), 1500 (s), 1437 (m), 1401 (m), 1316 (m), 1299 (m), 1251 (s), 1241 (s), 1181 (m), 1160 (m), 1105 (w), 1031 (s), 825 (s), 653 (w), 608 (w). NMR ($CDCl_3$, *δ*): ^{1}H, 9.42 (1H, br s, N*H*), 7.32 [4H, d, *J*(H–H) = 8.8 Hz, o-C*H*], 6.89 [4H, d, *J*(H–H) = 8.8 Hz, m-C*H*], 3.81 (6H, s, OCH_3).

(4-FPh)NNN(H)(4-FPh).[36] Prepared by method 1. Yield: 29% (2:1 hexane/EtOH). Mp: 112 °C. IR (KBr, cm^{-1}): 3183 (w), 1598 (w), 1505 (m), 1449 (m), 1398 (m), 1303 (w), 1225 (m), 1194 (s), 1116 (m), 838 (m), 828 (m), 653 (w), 606 (w). NMR ($CDCl_3$, *δ*): ^{1}H, 9.36 (1H, br s, N*H*), 7.35 (4H, m, m-C*H*), 7.06 (4H, m, o-C*H*); ^{19}F, −117.2 ($W_{1/2}$ = 12 Hz).

Table XVI. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3 Å^2) for (C_6F_5)NNN(H)(C_6F_5)

	x	*y*	*z*	*U*(eq)[a]
N(1)	1831(2)	106(2)	−131(2)	53(1)
N(2)	1019(2)	−435(2)	1294(2)	55(1)
N(12)	2095(2)	−133(2)	841(2)	50(1)
C(11)	2953(2)	536(3)	−617(2)	47(1)
C(12)	3021(3)	168(3)	−1629(2)	53(1)
F(12)	2069(2)	−665(2)	−2100(1)	77(1)
C(13)	4006(3)	627(3)	−2201(2)	61(1)
F(13)	4046(2)	239(2)	−3182(1)	91(1)
C(14)	4960(3)	1498(3)	−1748(2)	58(1)
F(14)	5927(2)	1984(2)	−2302(1)	81(1)
C(15)	4934(3)	1868(3)	−740(2)	55(1)
F(15)	5876(2)	2699(2)	−290(1)	83(1)
C(16)	3941(3)	1404(3)	−181(2)	51(1)
F(16)	3930(2)	1839(2)	793(1)	70(1)
C(21)	1173(2)	−614(3)	2368(2)	47(1)
C(22)	2092(3)	70(3)	3048(2)	50(1)
F(22)	2939(2)	961(2)	2703(1)	70(1)
C(23)	2154(3)	−124(3)	4099(2)	58(1)
F(23)	3057(2)	559(2)	4726(1)	87(1)
C(24)	1283(3)	−985(3)	4507(2)	59(1)
F(24)	1316(2)	−1167(2)	5553(1)	84(1)
C(25)	343(3)	−1652(3)	3852(3)	59(1)
F(25)	−534(2)	−2480(2)	4244(2)	94(1)
C(26)	311(3)	−1476(3)	2801(2)	53(1)
F(26)	−617(2)	−2158(2)	2172(1)	79(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(4-ClPh)NNN(H)(4-ClPh).[35] Prepared by method 2. Yield: 66% (1:1 hexane/EtOH). Mp: 125 °C. IR (KBr, cm^{-1}): 3191 (w), 1599 (m), 1507 (m), 1483 (m), 1438 (m), 1392 (m), 1303 (w), 1283 (w), 1243 (s), 1199 (m), 1174 (m), 1093 (m), 1010 (w), 826 (s), 589 (m), 504 (m). NMR ($CDCl_3$, *δ*): ^{1}H, 9.52 (1H, br s, N*H*), 7.32 (8H, s, o- and m-C*H*).

(4-BrPh)NNN(H)(4-BrPh). Prepared by method 2. Yield: 77% (2:3 hexane/EtOH). Mp: 136 °C. IR (KBr, cm^{-1}): 3192 (w), 1593 (m), 1506 (m), 1480 (m), 1437 (m), 1390 (m), 1302 (w), 1243 (s), 1198 (m), 1174 (m), 1070 (s), 1006 (m), 825 (m), 811 (w), 502 (w). NMR ($CDCl_3$, *δ*): ^{1}H, 9.52 (1H, br s, N*H*), 7.47 [4H, d, *J*(H–H) = 9.3 Hz, m-C*H*], 7.28 [4H, d, *J*(H–H) = 9.3 Hz, o-C*H*].

(C_6F_5)NNN(H)(C_6F_5).[37] Prepared by method 1, with the modification that concentrated HCl was used as the reaction solvent. Yield: 80% (heptane). Mp: 133 °C. IR (KBr, cm^{-1}): 3165 (w), 1546 (s), 1510 (s), 1468 (m), 1438 (w), 1415 (s), 1217 (s), 1041 (m), 988 (s), 975 (s), 891 (w), 813 (w), 790 (w), 761 (w), 693 (w), 666 (w), 606 (w), 566 (m). NMR ($CDCl_3$, *δ*): ^{1}H, 9.45 (br s, N*H*); ^{19}F, −150.9 ($W_{1/2}$ = 315 Hz, o-C*F*), −156.6 ($W_{1/2}$ = 233 Hz, m-C*F*), −162.2 ($W_{1/2}$ = 315 Hz, p-C*F*).

(Ph)NNN(H)(4-MeOPh).[35] Prepared by method 1, with the modification that aniline was diazotized in the presence of 10% excess HCl and then treated with a solution of 4-methoxyaniline hydrochloride in H_2O to give the unsymmetrical triazene compound. Yield: 77% (hexane). Mp: 184–85 °C. IR (KBr, cm^{-1}): 3173 (w), 3005 (w), 2935 (w), 1560 (s), 1500 (m), 1459 (s), 1440 (s), 1410 (s), 1312 (s), 1239 (s), 1192 (s), 1158 (m), 1106 (m), 1029 (s), 839 (s), 752 (m), 692 (m), 653 (m), 607 (m). NMR (C_6D_6, *δ*): ^{1}H, 9.10 (br s, N*H*), 7.55 [2H, d, *J*(H–H) = 8.2 Hz, o-C*H*, Ph], 7.08, 6.80 (7H, m, Ph, 4-MeOPh), 3.28 (3H, s, OCH_3).

Al[N(2-MePh)NN(2-MePh)]$_3$ (9). To a suspension of (2-MePh)NNN(H)(2-MePh)·(2-MePh)NH_2 (3.38 g, 10.2 mmol) in toluene (30 mL) was added $AlEt_3$ (5.0 mL, 1.0 M solution in hexane, 5.0 mmol). A clear yellow solution resulted in a yellow oil upon removal of the solvent under vacuum. The oil was triturated with hexane (30 mL) to produce a bright yellow crystalline solid, which was filtered off and dried under vacuum. Yield: 2.20 g, 93%. Toluene-free crystals were grown from hexane/CH_2Cl_2 (2:1) through selective evaporation of CH_2Cl_2 under vacuum. Mp: 176 °C. Anal. Calc for $C_{42}H_{42}AlN_9$: C, 72.08; H, 6.05; N, 18.01. Found: C, 71.42; H, 6.18; N, 17.72. IR (KBr, cm^{-1}): 2992 (w), 1512 (w), 1488 (m), 1459 (w), 1303 (m), 1276 (s), 1247 (m), 1211 (m), 757 (s), 714 (w), 668 (w). NMR ($CDCl_3$, *δ*): ^{1}H, 7.06 (2H, m,

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o-C*H*), 7.01 (6H, m, p-C*H*), 2.03 (6H, s, o-C*H*$_3$); ^{13}C, 143.5 (N*C*), 131.5, 130.4, 126.3, 125.4, 122.8 (*C*$_6$H$_4$), 19.5 (o-*C*H$_3$); ^{27}Al, 28 ($W_{1/2}$ = 1600 Hz).

Al[N(4-MePh)NN(4-MePh)]$_3$ (10). To a suspension of (4-MePh)NNN(H)(4-MePh) (1.69 g, 7.50 mmol) in hexane (30 mL) was added AlEt$_3$ (2.6 mL, 1.0 M in hexane, 2.6 mmol) via syringe. A deep orange precipitate formed, and the reaction mixture was refluxed gently for 30 min, whereupon all gas evolution had ceased. Afterward, the reaction mixture was cooled to room temperature and then placed in a freezer (–24 °C) overnight. Filtration, washing with pentane (20 mL), and vacuum-drying gave orange-yellow crystals. Yield: 1.57 g, 90%. Mp: 273 °C. Anal. Calc for $C_{42}H_{42}AlN_9$: C, 72.08; H, 6.05; N, 18.01. Found: C, 71.89; H, 6.06; N, 17.83. IR (KBr, cm^{-1}): 2919 (w), 1507 (s), 1303 (s), 1278 (s), 1248 (m), 1202 (m), 1177 (w), 821 (m), 771 (w), 662 (w), 623 (w), 566 (w), 512 (w). NMR (CDCl$_3$, δ): ^{1}H, 7.21 [4H, d, *J*(H–H) = 8.3 Hz, o-C*H*], 6.98 [4H, d, *J*(H–H) = 8.3 Hz, m-C*H*], 2.25 (6H, s, C*H*$_3$); ^{13}C, 157.7 (N*C*), 139.0, 119.4, 115.4 (*C*$_6$H$_4$), 54.9 (*C*H$_3$); ^{27}Al, 25 ($W_{1/2}$ = 1580 Hz).

Al[N(4-MeOPh)NN(4-MeOPh)]$_3$ (11). Prepared in a manner similar to that for **10** using (4-MeOPh)NNN(H)(4-MeOPh) (10.33 g, 40.2 mmol) and AlMe$_3$ (7.0 mL, 2.0 M solution in hexane, 14.0 mmol) to give an orange solid. Yield: 9.35 g, 84%. Mp: 261–263 °C. Anal. Calc for $C_{42}H_{42}AlN_9O_6$: C, 63.38; H, 5.32; N, 15.84. Found: C, 63.02; H, 5.21; N, 15.57. IR (KBr, cm^{-1}): 2957 (w), 2833 (w), 1505 (s), 1464 (w), 1440 (w), 1322 (m), 1293 (m), 1240 (s), 1179 (m), 1162 (s), 1033 (s), 831 (s), 662 (m), 618 (m), 559 (m). NMR (CDCl$_3$, δ): ^{1}H, 7.24 [4H, d, *J*(H–H) = 9.0 Hz, o-C*H*], 6.73 [4H, d, *J*(H–H) = 9.0 Hz, m-C*H*], 3.73 [6H, s, OC*H*$_3$]; ^{13}C, 142.3 (N*C*), 134.3, 129.9, 117.9 (*C*$_6$H$_4$), 20.9 (O*C*H$_3$); ^{27}Al, 27 ($W_{1/2}$ = 2460 Hz).

Al[N(4-FPh)NN(4-FPh)]$_3$ (12). Prepared in a manner similar to that for **10** using (4-FPh)NN(4-FPh) (1.74 g, 7.46 mmol) and AlEt$_3$ (2.5 mL, 1.0 M solution in hexane, 2.5 mmol) to give a brown-orange solid. Yield: 1.63 g, 91%. Mp: 258 °C. Anal. Calc for $C_{36}H_{24}AlF_6N_9$: C, 59.75; H, 3.34; N, 17.42. Found: C, 59.27; H, 3.37; N, 17.20. IR (KBr, cm^{-1}): 2552 (w), 1807 (w), 1502 (w), 1448 (w), 1320 (s), 1306 (s), 1286 (s), 1222 (s), 1197 (m), 1150 (m), 1097 (w), 863 (w), 834 (w), 661 (m), 617 (m), 565 (m), 514 (m), 449 (m). NMR (CDCl$_3$, δ): ^{1}H, 7.24 (4H, m, m-C*H*), 6.93 (4H, m, o-C*H*); ^{13}C, 160.0 [d, *J*(C–F) = 243 Hz, p-*C*F], 140.3 (s, N*C*), 119.2 [d, *J*(C–F) = 23 Hz, m-*C*H], 116.5 [d, *J*(C–F) = 6.3 Hz, o-*C*H]; ^{27}Al, 25 ($W_{1/2}$ = 1400 Hz); ^{19}F, –117.2.

Al[N(4-ClPh)NN(4-ClPh)]$_3$ (13). A solution of (4-ClPh)NNN(H)(4-ClPh) (4.00 g, 15.0 mmol) in toluene (30 mL) was treated with AlEt$_3$ (5.2 mL, 1.0 M hexane solution, 5.2 mmol). After 1.5 h of heating, the solvent was removed in vacuo to give a bright yellow-orange microcrystalline solid, which was washed with pentane (30 mL) and vacuum-dried. Yield: 3.73 g, 88% **13**·$^1/_4$$C_7H_8$. Solvent-free crystals of **13** suitable for X-ray analysis were obtained by recrystallization from pentane/CH_2Cl_2 (1:1). Mp: 239 °C. Anal. Calc for $C_{36}H_{42}AlCl_6N_9$: C, 52.58; H, 2.94; N, 15.33. Found: C, 52.24; H, 2.87; N, 15.19. IR (KBr, cm^{-1}): 1507 (s), 1311 (s), 1295 (s), 1273 (s), 1208 (w), 1093 (m), 1008 (w), 852 (w), 829 (s), 594 (w), 558 (w), 510 (w). NMR (CDCl$_3$, δ): ^{1}H, 7.19 (s, o- and m-C*H*); ^{13}C, 142.3 (N*C*), 131.2, 129.9, 119.1 (*C*$_6$H$_4$); ^{27}Al, 26 ($W_{1/2}$ = 1720 Hz).

Al[N(4-BrPh)NN(4-BrPh)]$_3$ (14). Prepared in a manner similar to that for **10**, using (4-BrPh)NNN(H)(4-BrPh) (4.25 g, 12.0 mmol) in toluene (50 mL) and AlEt$_3$ (4.1 mL, 1.0 M solution in hexane, 4.1 mmol) to give a bright orange, microcrystalline solid. Yield: 3.90 g, 88% **14**·$^1/_4$$C_7H_8$. Solvent-free, analytically pure **14** was obtained by dissolving in hexane/CH_2Cl_2 (1:1) and removing the more volatile CH_2Cl_2 under vacuum until crystallization was imminent. Mp: 260 °C. Anal. Calc for $C_{36}H_{24}AlBr_6N_9$: C, 39.70; H, 2.22; N, 11.57. Found: C, 39.26; H, 2.11; N, 11.36. IR (KBr, cm^{-1}): 1485 (s), 1438 (w), 1308 (s), 1293 (s), 1271 (s), 1207 (m), 1071 (s), 1006 (m), 848 (m), 825 (s), 564 (m), 505 (m). NMR (CDCl$_3$, δ): ^{1}H, 7.34 [4H, d, *J*(H–H) = 8.7 Hz, o-C*H*], 7.13 [4H, d, *J*(H–H) = 8.7 Hz, m-C*H*]; ^{13}C, 142.6 (N*C*), 132.9, 119.4, 119.1 (*C*$_6$H$_4$); ^{27}Al, 26 ($W_{1/2}$ = 1860 Hz).

Al[N(C_6F_5)NN(C_6F_5)]$_3$ (15). Prepared in a manner similar to that for **10** using (C_6F_5)NNN(H)(C_6F_5) (2.26 g, 6.70 mmol) and AlMe$_3$ (2.3 mL, 1.0 M solution in hexane, 2.3 mmol) to give a yellow-green solid. Yield: 1.84 g, 80%. Mp: 179 °C. Anal. Calc for $C_{36}AlF_{30}N_9$: C, 37.92; N, 10.91. Found: C, 39.01; N, 12.22. IR (KBr, cm^{-1}): 1530 (s), 1326 (w), 1284 (s), 1254 (m), 1221 (w), 1068 (w), 982 (s), 812 (w), 696 (w), 621 (w), 538 (w). NMR (CDCl$_3$, δ): ^{13}C, 141.4 [dd, ^{1}*J*(C–F) = 255 Hz, ^{2}*J*(C–F) = 10.5 Hz, o-*C*F], 140 [dt, ^{1}*J*(C–F) = 256 Hz, ^{2}*J*(C–F) = 14.3 Hz, p-*C*F], 138.0 [dt, ^{1}*J*(C–F) = 254 Hz, ^{2}*J*(C–F) = 13.9 Hz, m-*C*F], 118.4 [t, *J*(C–F) = 12.0 Hz, N*C*]; ^{27}Al, 34 ($W_{1/2}$ = 625 Hz); ^{19}F, –151.8 [d, *J*(F–F) = 19.9 Hz, o-C*F*], –155.4 [m, *J*(F–F) = 21.3 Hz, m-C*F*], –161.4 [t, *J*(F–F) = 19.9 Hz, p-C*F*].

Table XVII. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3 Å^2) for (2-MePh)NNN(H)(2-MePh)·(2-MePh)NH_2

	x	*y*	*z*	*U*(eq)[a]
N(1)	–738(5)	33(5)	–3822(4)	59(2)
N(12)	–1253(5)	1163(5)	–3703(4)	60(3)
N(2)	–164(5)	2276(5)	–2689(5)	64(3)
C(11)	–1887(7)	–1152(6)	–4883(5)	56(3)
C(12)	–3434(7)	–1046(6)	–5701(6)	66(3)
C(13)	–4505(7)	–2247(7)	–6683(6)	77(4)
C(14)	–4043(8)	–3540(7)	–6839(6)	82(4)
C(15)	–2509(8)	–3625(6)	–6034(6)	76(4)
C(16)	–1410(7)	–2445(6)	–5040(5)	61(3)
C(17)	232(7)	–2594(6)	–4182(6)	77(3)
C(21)	–560(7)	3609(6)	–2507(6)	59(3)
C(22)	–2016(7)	3815(6)	–3352(6)	72(4)
C(23)	–2336(8)	5159(8)	–3134(8)	88(4)
C(24)	–1208(10)	6289(7)	–2069(9)	96(5)
C(25)	219(9)	6058(6)	–1238(7)	79(4)
C(26)	590(7)	4735(6)	–1428(6)	64(4)
C(27)	2171(8)	4530(6)	–502(6)	82(4)
N(3)	2761(5)	934(5)	–1474(5)	71(3)
C(31)	3132(7)	931(5)	–140(6)	61(3)
C(32)	2074(8)	170(6)	44(8)	77(4)
C(33)	2429(12)	220(9)	1394(13)	114(7)
C(34)	3793(14)	1002(12)	2535(10)	128(8)
C(35)	4813(9)	1756(9)	2338(7)	103(5)
C(36)	4541(7)	1749(6)	1014(7)	70(4)
C(37)	5669(7)	2547(6)	801(7)	83(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Al[N(Ph)NN(4-MeOPh)]$_3$ (16). Prepared in a manner similar to that for **10** using (Ph)NNN(H)(4-MeOPh) (2.73 g, 12.0 mmol) and AlMe$_3$ (4.2 mL, 1.0 M solution in hexane, 3.4 mmol) to give a dark orange solid. A second washing with warm hexane was necessary to remove traces of unreacted ligand. Yield: 2.52 g, 89%. Mp: 163–165 °C. Anal. Calc for $C_{39}H_{36}AlN_9O_3$: C, 66.37; H, 5.14; N, 17.86. Found: C, 64.84; H, 5.19; N, 17.22. IR (KBr, cm^{-1}): 3053 (w), 2941 (w), 2833 (w), 1595 (w), 1583 (w), 1508 (m), 1488 (m), 1326 (s), 1310 (s), 1291 (s), 1253 (s), 1241 (s), 1210 (m), 1165 (m), 1034 (m), 830 (m), 756 (m), 688 (m), 679 (m), 558 (m). NMR (C_6D_6, δ): ^{1}H, 7.66 (6H, m, o-C*H*), 7.62 (6H, m, o-C*H*), 7.03 (6H, m, m-C*H*), 6.81 [3H, t, *J*(H–H) = 8.0 Hz, p-C*H*], 6.61 (6H, m, m-C*H*), 3.10 (3H, s, OC*H*$_3$), 3.09 (6H, s, OC*H*$_3$); ^{13}C, 158.2 (O*C*), 145.4, 145.3 (N*C*, Ph), 138.7, 138.6, 138.5 (N*C*, 4-MeOPh), 129.9, 124.9, 119.8, 118.2, 115.4 (Ph, 4-MeOPh), 54.9 (O*C*H$_3$); ^{27}Al, 26 ($W_{1/2}$ = 2530 Hz).

X-ray Crystallographic Studies. A crystal data summary is given in Table IX; fractional atomic coordinates are listed in Tables X–XVII. Crystals of compounds **1**, **6**, AlMe(salen), **9**, **11**, **13**, (C_6F_5)NNN(H)(C_6F_5), and 2-MePh)NNN(H)(2-MePh)·(2-MePh)NH_2 were mounted directly onto the goniometer with silicone grease. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[14] using a Nicolet R3m/v diffractometer operating in the θ–2θ scan mode. Data collection was controlled by using the Nicolet P3 program.[38] Empirical absorption corrections were applied to the data using the program PSICOR. Further experimental data are given in Table IX.

The structures were solved using the direct methods program XS, which revealed the position of most of the heavy atoms; the remainder were located using standard difference method techniques. Most, but not all, of the hydrogens were visible in the final difference mpa. Hydrogens were included as fixed atom contributors in the final cycles, *d*(C–H) = 0.96 Å and *U*(iso) = 0.08 Å^2. The hydrogen atom in (C_6F_5)NNN(H)(C_6F_5) was located in the electron density map and refined. The hydrogen atoms in (2-MePh)NNN(H)(2-MePh)·(2-MePh)NH_2 were all located in the electron density map and refined with

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(38) *P3/R3 Data Collection Manual*; Nicolet Instrument Corp.: Madison, WI, 1987.

a fixed thermal parameter, $U(\text{iso}) = 0.08$ Å^2. All hydrogen atoms were fixed in the final refinement. Since standard deviations are meaningless for N–H distances and X–N–H angles when the H atoms are included as invariants, they have been omitted from the text and Tables VII and VIII.

The difference Fourier map for compound **1** revealed two alternative positions for the methine and one methyl carbon of one of the isobutyl ligands. These were initially included in the refinement such that equivalent atoms were treated with linked thermal parameters and the group occupancies were constrained to total 1. The latter converged at values of 0.489(5) and 0.511(5) and were fixed at 0.5 for the final refinement. The disorder can be imagined as being due to inversion of the methylenic carbon. In this inversion, the methylene, C(31), and one of the methyls, C(33), remain fixed within the resolution of the experiment. Hydrogen atoms were given appropriate site occupancy factors.

Details of the refinements for all structures are given in Table IX. Atomic scattering factors and anomalous scattering parameters were as given in the literature.[39]

Acknowledgment. Financial support was provided in part by the National Science Foundation, the Aluminum Research Board, and the Harvard University Undergraduate Work-Study program. Professor R. M. Kren (University of Michigan—Flint) is acknowledged for providing the impetus for this work. Richard Miller (Akzo Chemicals) is gratefully acknowledged for the gift of $AlMe_3$ and $AlEt_3$.

Supplementary Material Available: Tables of bond distances, bond angles, anisotropic displacement coefficients, and hydrogen atomic coordinates (22 pages). Ordering information is given on any current masthead page.

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(39) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.